Suspended Particles in Outdoor and Indoor Air: Characterization to Support Epidemiological Studies

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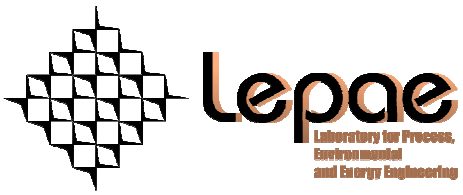

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Abstract

The assessment of the health impacts associated with exposure to particulate matter (PM) required more comprehensive information, mainly related to detailed physical-chemical characterisation of the respective particles. Thus this work studied the physical and chemical characterisation of suspended particles present in urban atmospheres (outdoor air) and in confined polluted environments (indoor air). The specific objectives were to study the influence of traffic emissions and of tobacco smoke on the physical and chemical characteristics in different fractions of inhalable particles with special attention to PM_{10} and $PM_{2.5}$, considering: PM concentrations and size distributions, elemental compositions, carbonaceous content, and the composition of polycyclic aromatic hydrocarbons (PAHs).

PM_{10} and $PM_{2.5}$ were collected using low-volume samplers at various sites influenced by traffic emissions and tobacco smoke as well at background (reference) sites used for the comparison, not being directly influenced by the respective emissions. The elemental analyses were performed by proton induced X-ray emission (PIXE) and scanning electron microscopy combined with X-ray microanalysis; carbonaceous components were determined by thermal combustion whereas PAHs were analysed by microwave assisted extraction (MAE) combined with liquid chromatography (LC).

The results showed that traffic emissions significantly increased the concentrations of PM_{10}, $PM_{2.5}$ and their metal contents. The elements originated mostly from anthropogenic activities were predominantly present in $PM_{2.5}$, whereas the elements mostly originated from crust predominantly occurred in $PM_{2.5-10}$. Regarding the carbonaceous content traffic emissions increased mainly the levels of elemental carbon being 500-900% and 490-740% higher for PM_{10} and $PM_{2.5}$, respectively. When influenced by traffic emissions the total concentration of nine carcinogenic PAHs increased by 2400% and 3000% in PM_{10} and $PM_{2.5}$, respectively, being mainly present in $PM_{2.5}$; these nine carcinogenic compounds represented 68% and 74% of total PAHs for PM_{10} and $PM_{2.5}$, respectively.

Tobacco smoke significantly increased PM_{10} and $PM_{2.5}$ concentrations being higher for $PM_{2.5}$. The total concentrations of five carcinogenic elements (Cr, Ni, As, Cd and Pb) were 1100-3500% higher for PM_{10} and 840-2200% higher for $PM_{2.5}$, being predominantly present in $PM_{2.5}$; tobacco smoke increased mainly the levels of organic carbon being 290-500% and 300-590% higher for PM_{10} and $PM_{2.5}$, respectively. Considering the carcinogenic PAHs the increase was 780% and 770% in PM_{10} and $PM_{2.5}$, respectively; nine carcinogens compounds represented, respectively, 56% and 55% of total PAHs in PM_{10} and $PM_{2.5}$. All PAHs (including the carcinogenic ones) were mainly present in $PM_{2.5}$, which corresponds to a strong risk for cardiopulmonary disease and lung cancer.

Considering that carcinogenic components were predominantly present in particles of smaller sizes, the obtained conclusions confirm the strong risks associated with exposure to traffic emissions and tobacco smoke. The results obtained in this work are relevant for development of strategies to protect public health and to support future epidemiological studies evaluating passive smokers and populations affected by traffic emission sources.

Sumário

A avaliação dos impactos na saúde associados à exposição a partículas em suspensão (PM) necessita de informação mais detalhada e completa sobre a sua composição físico-química. Assim, este trabalho dedicou-se à caracterização física e química das partículas em suspensão presentes em atmosferas urbanas (ar exterior) e em ambientes confinados poluídos (ar interior). Os objectivos específicos foram o estudo da influência das emissões do tráfego automóvel e das emissões do fumo do tabaco sobre as características físicas e químicas das diferentes fracções de partículas inaláveis com especial atenção para as PM_{10} e $PM_{2.5}$, considerando: concentração e distribuição de tamanhos, composição elementar, conteúdo em carbono elementar e carbono orgânico e a composição em hidrocarbonetos aromáticos policíclicos (HAPs).

As PM_{10} e $PM_{2.5}$ foram recolhidas, utilizando amostradores de baixo volume, em vários locais influenciados pelas emissões do tráfego e pelo fumo do tabaco, bem como em locais de referência não directamente influenciados pelas respectivas emissões. A análise elementar das PM foi realizada pelas técnicas de emissão de protões induzida por raios-X (PIXE) e microscopia electrónica de varrimento (SEM) combinada com microanálise por raios-X (EPMA); o conteúdo em carbono elementar e carbono orgânico foi determinado por combustão térmica e os HAPs foram analisados por extracção assistida por micro-ondas (MAE), combinada com cromatografia líquida (LC).

Os resultados mostraram que as emissões do tráfego aumentaram significativamente as concentrações de PM_{10} e $PM_{2.5}$, bem como o conteúdo metálico das respectivas fracções. Os elementos com origem antropogénica foram predominantemente encontrados nas $PM_{2.5}$, enquanto os elementos provenientes da crosta terrestre ocorreram predominantemente nas $PM_{2.5-10}$. As emissões do tráfego aumentaram principalmente os níveis de carbono elementar sendo 500-900% e 490-740% superiores para as PM_{10} e $PM_{2.5}$, respectivamente. Quando influenciadas pelas emissões do tráfego a concentração total de nove HAPs com elevado potencial cancerígeno aumentou 2400% e 3000% nas PM_{10} e $PM_{2.5}$, respectivamente, estando principalmente presentes nas $PM_{2.5}$; estes nove HAPs representaram 68% e 74% do total de HAPs nas PM_{10} e $PM_{2.5}$, respectivamente.

O fumo do tabaco aumentou significativamente as concentrações de PM_{10} e $PM_{2.5}$, sendo este aumento maior para as $PM_{2.5}$. As concentrações totais de cinco elementos com elevado potencial carcinogénico (Cr, Ni, As, Cd e Pb) foram 1100-3500% maiores para as PM_{10} e 840-2200% maiores para as $PM_{2.5}$, encontrando-se predominantemente nas $PM_{2.5}$, o fumo do tabaco aumentou principalmente os níveis de carbono orgânico sendo 290-500% e 300-590% superior para as PM_{10} e $PM_{2.5}$, respectivamente. Considerando os HAPs com elevado potencial carcinogénico, o aumento foi de 780% e 770% nas PM_{10} e $PM_{2.5}$, respectivamente, estes nove HAPs representaram respectivamente, 56% e 55% do total de HAPs nas PM_{10} e $PM_{2.5}$. Todos os HAPs (incluindo os carcinogénicos) estavam principalmente presentes nas $PM_{2.5}$, o que corresponde a um forte risco para doenças cardio-pulmonares e cancro do pulmão.

Considerando que os componentes carcinogénicos estiveram predominantemente presentes nas partículas de menores dimensões, as conclusões obtidas confirmam os fortes riscos associados à exposição ao fumo do tabaco e às emissões do tráfego. Os resultados obtidos neste trabalho são relevantes para o desenvolvimento de estratégias para proteger a saúde pública e para apoiar futuros estudos epidemiológicos avaliando os fumadores passivos e as populações afectadas pelas emissões do tráfego.

Résumé

L'évaluation des impacts sur la santé associés à l'exposition aux particules en suspension (PM) nécessite plus d'informations détaillées et complètes sur leur composition physico-chimique. Ce travail est dédié à la caractérisation physique-chimique des particules dans les atmosphères urbaines (air extérieur) et dans des milieux pollués (air intérieur). Les objectifs spécifiques sont d'étudier l'influence des émissions du trafic et des émissions de la fumée de tabac sur les caractéristiques physiques et chimiques des différentes fractions de particules inhalables avec une attention particulière à la PM_{10} et $PM_{2.5}$, en tenant compte: la concentration et la distribution de taille, la composition élémentaire, la teneur en carbone élémentaire et le carbone organique et la composition de les hydrocarbures aromatiques polycycliques (HAPs).

PM_{10} et $PM_{2.5}$ ont été recueillies au moyen d'échantillonneurs à faible volume sur divers sites influencée par les émissions du trafic et de la fumée de tabac, ainsi que des sites de référence qui ne sont pas directement influencés par leurs émissions. L'analyse élémentaire des PM été faite par les techniques d'émission de photons X induite par protons (PIXE) et la microscopie électronique à balayage (MEB) en combinaison avec X-ray micro-analyse; la teneur en carbone élémentaire et le carbone organique a été déterminée par la combustion thermique et les HAPs ont été analysés par extraction assistée par micro-ondes (MAE), combinée avec la chromatographie en phase liquide (CPL).

Les résultats ont montré que les émissions du trafic ont augmenté de manière significative les concentrations de PM_{10}, $PM_{2.5}$, ainsi que la teneur en métaux de leurs fractions. Les éléments d'origine anthropique ont été principalement trouvés dans les $PM_{2.5}$, tandis que les éléments de la croûte terrestre se sont produits principalement dans les $PM_{2.5-10}$. Les émissions de trafic ont augmenté principalement les niveaux de carbone élémentaire de 500-900% et de 490-740% plus élevé pour les PM_{10} et $PM_{2.5}$, respectivement. Lorsque influencée par les émissions du trafic la concentration totale en de neuf HAPs avec haut potentiel cancérogène a augmenté de 2400% et 3000% en PM_{10} et $PM_{2.5}$, respectivement, sont principalement présents dans les $PM_{2.5}$, ces neuf composés carcinogènes représenté 68% et 74% des HAPs totaux pour les PM_{10} et $PM_{2.5}$, respectivement.

La fumée du tabac a augmenté de manière significative les concentrations de PM_{10} et $PM_{2.5}$, qui est plus élevé pour les $PM_{2.5}$. La concentration totale de cinq éléments à fort potentiel carcinogène (Cr, Ni, As, Cd et Pb) ont été de 1100-3500% plus élevés pour les PM_{10} et de plus de 840-2200% pour les $PM_{2.5}$, concentration qui se trouve principalement dans les $PM_{2.5}$, la fumée de tabac a augmenté les niveaux de carbone organique de 290-500% et 300-590% plus élevé pour les PM_{10} et $PM_{2.5}$, respectivement. En ce qui concerne les HAPs carcinogènes, l'augmentation a été de 780% et 770% en PM_{10} et $PM_{2.5}$, respectivement, neuf composés cancérigènes représenté respectivement 56% et 55% du total des HAPs dans les PM_{10} et $PM_{2.5}$. Tous les HAPs (compris les carcinogènes) étaient principalement présentes dans les $PM_{2.5}$, ce qui est un fort risque pour l´existence des maladies cardio-pulmonaires et du cancer du poumon.

Considérant que les composants carcinogènes sont essentiellement présents dans les plus petites particules, les résultats confirment le forte des risques associés à l'exposition à la fumée de tabac et les émissions du trafic. Les résultats dans ce travail sont pertinents pour l'élaboration de stratégies visant à protéger la santé publique et d'appuyer de futures études épidémiologiques évaluant le tabagisme passif et les populations touchées par la pollution de trafic.

For Mum,
For Sis,
With my love.

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List of Publications

Most of the content presented in this thesis was published, accepted or submitted for publication in:

Chapters in book

1. M. C. M. Alvim-Ferraz, M. C. Pereira, K. Slezakova, Partículas Suspensas no Ar Exterior e Interior: Caracterização para Suporte de Estudos Epidemiológicos, *in Investigação em Ambiente e Saúde: Desafios e Estratégias* (C. A. Borrego et al., Eds.), Universidade de Aveiro, 41-45, Aveiro 2009.
2. K. Slezakova, M. A. Reis, M. C. Pereira, M. C. M. Alvim-Ferraz, Influence of Traffic on the Elemental Composition of PM_{10} and $PM_{2.5}$ in Oporto Region, *in Air Pollution XV, WIT Transactions on Ecology and the Environment* (C. A. Borrego, C. A. Brebbia, Eds.), WIT Press, Vol. 101, 59-68, Southampton 2007.

Articles in Scientific Journals included in *"Scientific Citation Index"*

1. K. Slezakova, M. C. Pereira, J. C. M. Pires, F. G. Martins, M. C. M. Alvim-Ferraz, The Use of SEM to Identify Tobacco Smoke Components in Breathable Particles of Different Sizes, *submitted*.
2. K. Slezakova, D. Castro, M. C. Pereira, S. Morais, C. Delerue-Matos, M. C. M. Alvim-Ferraz, Influence of Tobacco Smoke on Carcinogenic PAH Composition in Indoor PM_{10} and $PM_{2.5}$, *Atmospheric Environment,* **43**, 6376-6382, 2009.
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2. D. Castro, K. Slezakova, C. Delerue-Matos, M. C. Alvim-Ferraz, S. Morais, M. C. Pereira, Contribution of Traffic and Tobacco Smoke in the Distribution of Polycyclic Aromatic Hydrocarbons on Outdoor and Indoor $PM_{2.5}$, *11th International Conference on Environmental Science and Technology*, A131-137, Crete, September 2009.
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Nomenclature

Abbreviations

ASTDR	Agency for Toxic Substances and Disease Registry
Bc	Background monitoring site
CA	Cluster analysis
EC	European Community
EDS	Energy dispersive spectrometer
EEA	European Environment Agency
EF / EFs	Enrichment factor / factors
ETS	Environmental tobacco smoke
EU	European Union
FLD	Fluorescence detection
IARC	International Agency for Research on Cancer
LC	Liquid chromatography
MAE	Microwave assisted extraction
NDIR	Nondispersive infrared spectrophotometer
PAD	Photodiode array detection
PAH / PAHs	Polycyclic aromatic hydrocarbon / hydrocarbons
PIXE	Proton induced X-ray emission
PM	Particulate matter
PM_{10}	Particulate matter which passes through a size-selective inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter
$PM_{2.5}$	Particulate matter which passes through a size selective inlet with a 50% efficiency cut-off at 2.5 μm aerodynamic diameter
$PM_{2.5-10}$	PM_{10} fraction without $PM_{2.5}$

PTFE	Polytetrafluoroethylene
Rf	Reference site (not influenced by tobacco smoke)
SEM	Scanning electron microscopy
TEF	Toxicity equivalency factor
Tr	Monitoring site influenced by traffic emissions
Ts	Monitoring site influenced by tobacco smoke
USEPA	U.S. Environmental Protection Agency
WHO	World Health Organization

Greek symbols

ρ	Particle density [pg μm^{-3}]
χ	Shape factor
Σ	Sum

Roman symbols

Al	Aluminium
As	Arsenic
Ba	Barium
Br	Bromine
C	Carbon
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Cl	Chlorine
Co	Cobalt
Cr	Chromium

Cu	Copper
D_{ae}	Aerodynamic diameter [μm]
D_{phys}	Physical diameter [μm]
F	Fluorine
Fe	Iron
I	Iodine
K	Potassium
La	Lanthanum
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
Ni	Nickel
P	Phosphorus
Pb	Lead
R	Correlation coefficient
S	Sulfur
Sb	Antimony
Se	Selenium
Si	Silicon
Sn	Tin
Ti	Titanium
V	Vanadium
Zn	Zinc

Subscripts

E	Refers to elements
PAHs	Refers to polycyclic aromatic hydrocarbons

1. Preface

1.1 Relevance and motivation

The work reported in this thesis, “Suspended Particles in Outdoor and Indoor Air: Characterization to Support Epidemiological Studies”, was related with the physical and chemical characterisation of the different fractions of inhalable particles present in ambient air and in confined environments.

The work was divided into two main sections. The first part aimed to study the influence of traffic emissions on the physical and chemical characteristics of particulate matter. The second part of the work dealt with the characterisation of indoor particles originated from tobacco smoke.

The health risks associated with exposure to atmospheric pollution are one of the major concerns of European Union. Kunzli and collaborators estimated that only in 3 European countries, about 40 000 people died annually due to the effects of atmospheric pollution (Kunzli et al., 2000). In Europe, hundred of thousands premature deaths are annually attributed to atmospheric pollution, and the adverse impacts of long-term exposure to particles appear to be a very important public health problem.

Particulate matter (PM) is a mixture of solid or solid/liquid particles suspended in air. Upon inhalation, particles with aerodynamic diameter smaller than 10 μm (PM_{10}) enter the lower

respiratory tract, while gas exchange regions of lungs are penetrated by particles smaller than 2-3 μm ($PM_{2.5}$) (Brunekreef and Holgate, 2002). The scientific evidence showed that the exposure to ambient levels of PM_{10} and $PM_{2.5}$ leads to increase morbidity and mortality rates, caused by pulmonary and cardiovascular diseases (Dockery and Pope, 1994). Nevertheless, the mechanisms of these adverse health effects are not fully understood yet. Originally, it was believed that the size of the particles was the most influential parameter for the health effects, as it determines the place of particle deposition in respiratory tract. However, the recent evidence suggests that chemical composition of atmospheric particles is also a significant contributor to these adverse health effects (Harrison and Yin, 2000; Pérez et al., 2007; Viana et al., 2008).

Chemical composition of particulate matter is a very complex topic. The particles are influenced by emissions from different sources, so their composition is very heterogeneous (Maynard and Howard, 1999). The current information on PM chemical composition is still limited, namely concerning the quantification of toxic components such as heavy metals and polycyclic aromatic hydrocarbons. As it is necessary to identify the role of particle components on the respective health effects, the detailed characterisation of particulate matter is needed, namely related to anthropogenic sources that are most likely to contain these toxic substances.

In Metropolitan Area of Oporto city, the components of higher toxicity were found in the fractions of smaller dimensions (Alvim Ferraz et al., 1988; Alvim Ferraz, 1996). Despite that, the network of air quality measurements has been mostly limited to the quantification of PM_{10} fraction, having numerous exceedances of the limit values from European Directives (EEA, 2003; Salcedo et al., 1999; Pereira et al., 2005; Alvim-Ferraz et al., 2005). Facing the existent information and to protect the public health, the establishment of $PM_{2.5}$ limits has become absolutely essential. European Union has recognised the importance of this subject and in recent Directive 2008/50/EC on ambient air quality (EU Directive, 2008) it has promulgated a $PM_{2.5}$ annual limit standard. Nevertheless, the knowledge in this area is still limited and the number of subjects within this directive will be re-evaluated in 2013. In order to support the establishment of new concentration limits, the scientific community should develop further knowledge, including the detailed characterisation of different fractions of PM_{10} with special attention to $PM_{2.5}$.

Traffic emissions are one of the most health-relevant sources of particles, as the epidemiological evidence has indicated that particles from these emissions are more toxic than others (Katsouyanni et al., 2001). In Europe, traffic emissions are one of the most important sources of particles (EEA, 2008). Thus, to fully protect the public health it is absolutely necessary to further understand the impacts of traffic emissions on health, and the proper evaluation of these impacts presumes the detailed physical-chemical characterisation of different size fractions of traffic related particles.

Until these days, some efforts have been made to protect population from exposure to outdoor particulate pollution. Still, about 90% of their time people spend indoors (homes, offices, restaurants), and the pollutants generated from the respective sources may lead to higher levels of harmful exposures, compared to outdoor ones. In order to protect public health the sources of harmful indoor air pollutants have to be considered, among those, tobacco being one of the greatest sources of indoor particles (WHO, 2000). To continue the assessment of the health impacts associated with exposure to tobacco smoke, more comprehensive information is required, mainly related to detailed physical-chemical characterisation of the respective particles.

Even the relatively low concentrations of particulate pollution can cause adverse health effects, hence the need for further reduction of this pollution. However, the limited knowledge on PM implies further difficulties for establishment of strategies to manage the air quality aiming the protection of public health. As the abatement of particulate pollution results in gains for public health, it is vital to develop strategies to reduce the concentrations of particles in both outdoor and indoor air. It is absolutely necessary to identify which PM fractions have the most relevant effects on human health, namely considering the toxic and carcinogenic content emitted by traffic and associated with tobacco smoke.

1.2 Objectives

In order to support the establishment of the limits for the concentrations of inhalable particles of smaller sizes present in indoor and outdoor air, and to develop strategies to reduce air pollution and to protect public health, the main objectives of this work were:

- The physical and chemical characterisation of suspended particles present in urban atmospheres (outdoor air) and in confined polluted environments (indoor air).

- The monitoring of indicator pollutants for traffic emissions and tobacco smoke (i.e. metals, carbonaceous species, and polycyclic aromatic hydrocarbons) in different fractions of inhalable particles with special attention to PM_{10} and $PM_{2.5}$.

- The support for epidemiological studies to evaluate the health impact of respirable particles, associated with traffic emissions and tobacco smoke.

The specific objectives of this work were:

1. To study the influence of traffic emissions on PM_{10} and $PM_{2.5}$ characteristics, considering:
    a. concentration and size distribution;
    b. bulk elemental composition;
    c. morphology and elemental composition of individual particles;
    d. carbonaceous composition;
    e. composition of polycyclic aromatic hydrocarbons.
2. To study the influence of tobacco smoke on PM_{10} and $PM_{2.5}$ characteristics, considering:
    a. concentration and size distribution;
    b. bulk elemental composition;
    c. morphology and elemental composition of individual particles;
    d. carbonaceous composition;
    e. composition of polycyclic aromatic hydrocarbons.

1.3 Thesis outline

The thesis is divided into five chapters. The content of each chapter is given below.

Chapter 1 (present chapter) is the preface of the thesis. It explains the relevance and motivation of the work as well as its objectives.

In **Chapter 2** a brief overview of the problematic related to particulate matter is given, covering its definitions, sources, and impact on human health. The chemical composition is also discussed as well as the specific characteristics of indoor particulate matter.

Chapter 3 provides the materials and methods used for this work. It describes the details of sampling sites and sampling procedures for collection of outdoor and indoor suspended particles. All analytical methods used to determine the selected chemical components of PM are also described.

Chapter 4 considers the results and discussions of the work. The first part of the chapter deals with suspended particles from outdoor air, the second part of the chapter is related to particulate matter found indoors. A brief comparison between indoor and outdoor PM is given in the last part of the chapter.

The conclusions of the thesis and the suggestions for future work are addressed in **Chapter 5**.

1.4 References

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2. Particulate matter: an overview

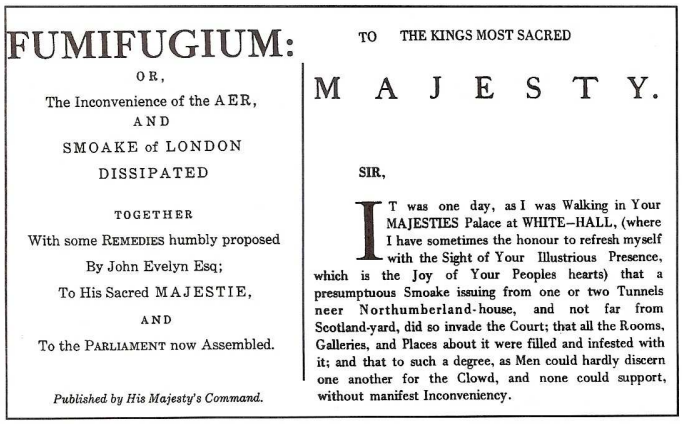
Air pollution is one of the most discussed topics nowadays. Being outdoors or indoors, ultimately we are surrounded by air and we essentially need air for living. During the last three decades the understanding of air pollution and its influence on health and environment has increased, but as already referred, the actual knowledge is still limited. Particulate matter is one of the most recently discussed pollutants. Its presence in the atmosphere has harmful effects on both human health and the environment, being at this moment a great concern around the world. Particulate matter has a broad scope and many volumes are needed to cover its different aspects. In this chapter, a brief discussion on the different aspects of particulate matter is given, covering its definitions, sources, and impact on human health. The chemical composition of particulate matter is also discussed as well as the specific characteristics of indoor particulate matter.

2.1 Historical overview

The existence of unpleasant and harmful particles in outdoor and indoor atmospheres followed human kind since the birth of civilisation. In fact, when man discovered fire, blessing as well as a curse came to humanity as fire generates smoke, the first anthropogenic air pollutant that has been also associated with the presence of particles. The very early literature refers to effects of smoke-related air pollution that became severe enough to report the situation: the Romans complained of the foul air in ancient Rome when Seneca described

"the heavy air" and "the stink of the smoky chimney thereof" (Peavy et al., 1985; Spurny, 1999).

To show the evolution of air particulate pollution, Great Britain is an excellent example, clearly demonstrating that during previous centuries several attempts were made to point out the significance of increasing air pollution. In 1273 in London the seriousness of particulate pollution led to the prohibition of sea-coal burning by King Edward I (1272-1307) who was bothered by mixtures of fog and smoke that appeared over London area; in 1306 his Royal Proclamation followed (Spurny, 1999). Despite these efforts the air quality in London grew bad as Londoners, due to heavy deforestation, more and more depended on use of coal. By the end of reign of Queen Elizabeth I (1558-1603) a law was passed prohibiting the coal burning when Parliament was sitting. This law was apparently passed due to personal preference, as it is believed that the Queen was allergic to smoke as well as she had aversion to it; she moved out of London to reside in cleaner-air countryside and this particular law allowed her to return to London when her presence was necessary. Over a century later, in 1661 improvement of air quality was not still achieved when the first major tract regarding the particulate pollution was submitted to King Charles II by diarist John Evelyn (Spurny, 1999). Evelyn's "Fumifugium: or the Inconvenience of the Aer and Smoake of London Dissipated" contained description of the pollution in London as well as the recommendations for improvements (Figure 2.1). Evelyn suggested removing all smoke-producing plants from London and the planting of greenbelts around the city, two key solutions that have been still recommend today (Peavy et al., 1985). He also recognised that certain individuals would be confronted by higher exposure to pollutants by virtue of their trade, and argued that people should not commend such high exposures. Furthermore, Evelyn pointed out that some individuals could be particularly sensitive to pollutants in the air and might never feel well in the cities, though majority of people showed little effects. This booklet has been reprinted often and it illustrates the degree to which Evelyn was concerned with air pollution. Unfortunately, as he fought for cleaner air without any regard to economic reality, his well-meaning plan was doomed to failure.



FUMIFUGIUM:

OR,

The Inconvenience of the AER,
AND
SMOAKE of LONDON
DISSIPATED

TOGETHER
With some REMEDIES humbly proposed
By John Evelyn Esq;
To His Sacred MAJESTIE,
AND
To the PARLIAMENT now Assembled.

Published by His Majesty's Command.

TO THE KINGS MOST SACRED

M A J E S T Y.

SIR,

IT was one day, as I was Walking in Your MAJESTIES Palace at WHITE-HALL, (where I have sometimes the honour to refresh myself with the Sight of Your Illustrious Presence, which is the Joy of Your Peoples hearts) that a presumptuous Smoake issuing from one or two Tunnels neer Northumberland-house, and not far from Scotland-yard, did so invade the Court; that all the Rooms, Galleries, and Places about it were filled and infested with it; and that to such a degree, as Men could hardly discern one another for the Clowd, and none could support, without manifest Inconveniency.

Figure 2.1 Title page of Fumifigium by John Evelyn (Spurny, 1999).

Throughout the eighteen and nineteen centuries it is likely that concentrations of particles in air increased as various industrial process expanded. It is rather interesting that high concentrations of particles in air also influenced the fashion and business (Holgate et al., 1999C). Women in England did not favour white colour because clothing became soiled as it hung to dry after being washed, umbrellas were used mainly in black colour to allow the protection from ink-colour rain. Buildings suffered too, and some of them required to be repainted every three years to hide the effects of blackening. Still the air pollution problems continued, although the interest in public health was broad, and some attempts to improve the air quality were done.

The problems surfaced greatly during the first half of the twentieth century when several air pollution episodes occurred around the world, being associated with particulates from industrial emissions and vehicle fuels and leading to premature death of hundreds of people. In 1952 these episodes escalated in "London disaster" (Mayor of London, 2002). On Thursday, December 4 a temperature inversion was created with fog settling over London area. The levels of particles and sulfur dioxide rose due to the use of coal for power and heating systems. As the high pressure area stalled, both particles and sulfur dioxide reached exceptional concentrations since there was no free air to disperse the smog. By the noon of December 5 smoke concentrations (i.e. particles) risen from 0.49 to 2.46 mg m^{-3} and they continued to rise up to 4.46 mg m^{-3} on 8 December (Mayor of London, 2002); the previous year the mean smoke concentrations during these days were between 0.12-0.44 mg m^{-3} (Mayor of London, 2002). The episode lasted till December 9 when the fog lifted up. Later on, it was estimated that between 3500 and 4000 deaths due to respiratory (mainly bronchitis

and emphysema) and cardiovascular diseases were attributed to this episode of air pollution, which included elderly and people with chronic respiratory problems, young children, but also otherwise healthy person whose work kept them outside. Regrettably, this great number of deaths had to be achieved to finally take action: in 1956 the Britons passed the Clean Air Act, the first significant legislative step toward reduction of air pollution.

During last three decades special efforts have been made in Europe, aiming to reduce air pollution and, more importantly, aiming to reduce the adverse impacts of atmospheric pollutants. Although these efforts led to a reduction of risks and effects, air pollution in Europe is still a matter of concern, mainly to relative impacts on the human health and on the environment. These impacts are considered as environment and health priorities in the European Union (EU), the exposure to particulate matter being one of the main issues related to the impact on human health.

2.2 Definitions

Particulate matter (PM) is a mixture of solid or solid/liquid particles suspended in air (WHO, 2000). These particles vary considerably in origin, size, shape, and in chemical properties. It is not very useful, nor does the technology exist to describe every aspect of these properties. Thus, it is common to classify the particles by their aerodynamic characteristics that govern the transport and removal from the air, the deposition within the respiratory system, and at least are partly associated with the chemical composition and sources of particles (WHO, 2000). The aerodynamic characteristics are usually summarised by the aerodynamic diameter (D_{ae}), a diameter of a spherical particle with a density of 1 g cm^{-3} that has the same inertial properties and settling velocity as the particle in question (Wilson et al., 2002). In other terms, aerodynamic diameter provides a simple mean to categorise the sizes of particles with different shapes and densities by a single dimension parameter.

2.3 Classification systems

The aerosol community uses several approaches in the classification of particles based on particle size, being measured in micrometres (μm). The particles of the major interest in air pollution studies usually range from 0.01 to 100 μm (Figure 2.2).

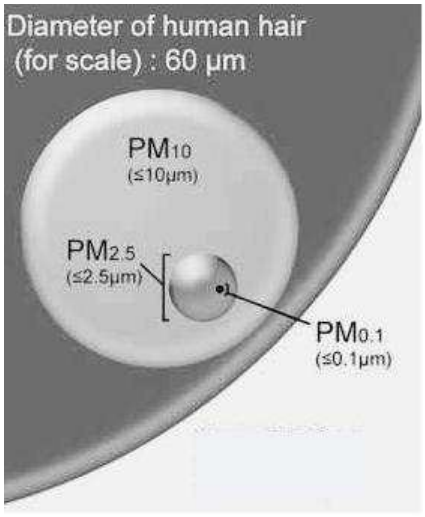


Figure 2.2 Comparison of particles with different aerodynamic diameters in relation to a human hair. PM_{10} represents a particle with aerodynamic diameter less or equal to 10 µm, $PM_{2.5}$ and $PM_{0.1}$ represent particles with aerodynamic diameter smaller than 2.5 and 0.1µm, respectively (USEPA, 2006).

The classification systems of airborne particles are (Wilson et al., 2002):

- modal classification: based on the observed size distributions and formation mechanisms;
- sampler cutpoint classification: usually based on the 50% cutpoint of the specific sampling device;
- occupational sizes: based on the entrance into various compartments of the respiratory system;
- regulatory sizes: based on regulatory sizes for air quality standards.

Modal classification, proposed by Whitby (Whitby, 1978**),** is based on the size distributions of PM into two principal groups - the coarse and fine mode.

The coarse mode consists of particles with aerodynamic diameter greater than the minimum in the particle mass distribution, which generally occurs between 1-3 µm (Wilson et al., 2002) (Figure 2.3). Those particles are usually the result of grinding activities and can include wind-blown dust from agricultural processes, unpaved roads, uncovered soils or mining operations. Pollen and spores also belong to this mode as do particles from plant fibres and leaves.

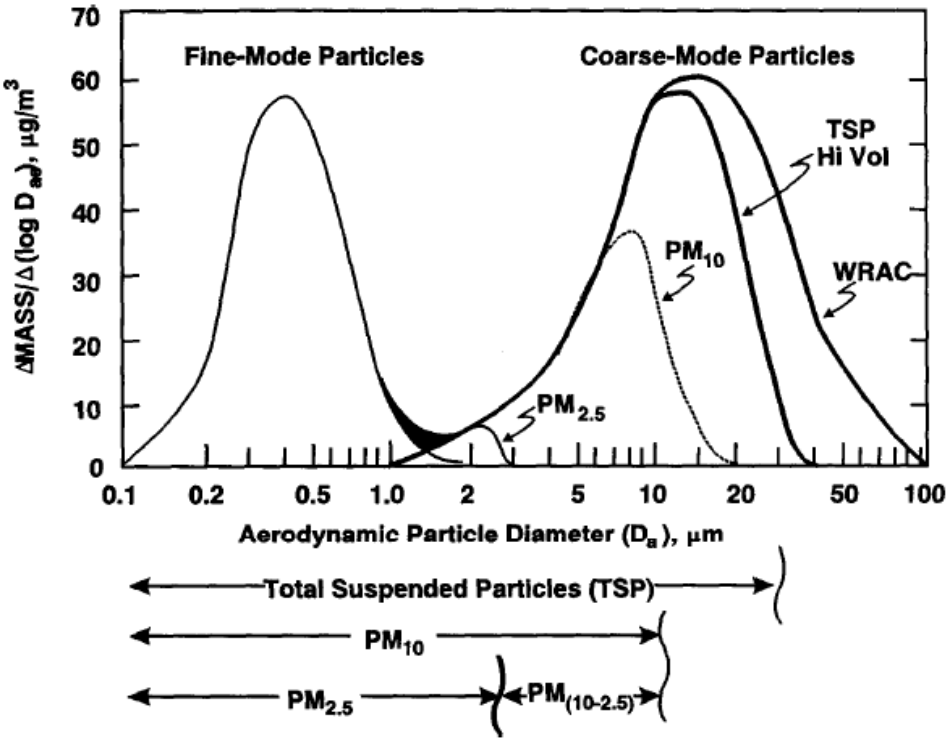


Figure 2.3 Schematic representation of the size distribution of particulate matter in ambient air (Wilson et al., 2002).

The fine mode consists of particles with aerodynamic diameter mostly smaller then minimum in the particle mass distribution (Figure 2.3), and is subdivided into two other ranges, based on the formation mechanisms of the particles (WHO, 2000):

- Nuclei mode (Oberdörster et al., 1995): also often called as "ultrafine particles" consists of particles with aerodynamic diameter smaller than 0.1 μm, that are directly emitted from combustion sources or formed by nucleation, that is, condensation of low-vapour-pressure substances formed by high temperature vaporisation or by chemical reactions in the atmosphere to form new particles (nuclei).

- Accumulation mode (Wilson et al., 2002): consists of particles with aerodynamic diameter between 0.1-1.0 μm. These particles are formed from nuclei-mode ones that grow by coagulation (i.e. the combination of two or more particles to form a larger particle) or by condensation (i.e. condensation of gas or vapour molecules on the surface of existing particles). Coagulation is most efficient for large numbers of particles, and condensation is most efficient for large surface areas.

> Therefore, the efficiency of both coagulation and condensation decreases as particle size increases, which effectively produces an upper limit such that particles do not grow by these processes beyond approximately 1 μm. Thus particles tend to "accumulate" between 0.1 and 1 μm, the so-called accumulation range. Describing above, it is then concluded that accumulation-mode particles normally do not grow in the coarse mode.

As mentioned previously the border between coarse and fine mode is between 1-3 μm (see Figure 2.3). Over the time the terms "fine" and "coarse", as applied to the particle sizes, have lost the precise meaning defined by Whitby. In many given articles, and also for the purposes of this work, the definition border is fixed by convention at 2.5 μm of aerodynamic diameter due to the measurement facilities.

The **sampler cutpoint** classification system (Maynard and Howard, 1999) comes from considerations of size-selective sampling, which has arisen in an effort to measure and study particle size fractions with some special significances (e.g., health, visibility, source apportionment) (Peavy et al., 1985). The size-selective sampling refers to the collection of particles below or within a specified aerodynamic size range, usually defined by the upper 50% cutpoint size. Accordingly, PM_{10} can be defined as particles, which pass through a size-selective inlet with a 50% efficiency cut-off at 10 μm of aerodynamic diameter (EU Directive, 1999).

The occupational health community has defined particle size fractions for use in the **protection of human health**. This system classifies particles according to their entrance into various compartments of the respiratory system into (WHO, 2000):

- inhalable particulate matter;
- thoracic particulate matter;
- respirable particulate matter.

While inhalable particles enter the respiratory system, including the head airways, thoracic particles travel past the larynx depositing in the lower respiratory tract; respirable particles are a subgroup of thoracic particles that penetrate to the deeper parts of lungs (WHO, 2000) (Figure 2.4). Although the terms are not completely equal, in literature thoracic particles

usually correspond to PM_{10} (particles with aerodynamic diameter smaller than 10 μm), while respirable particles typically correspond to $PM_{2.5}$ (particles that are smaller than 2.5 μm in aerodynamic diameter) (Brunekreef and Holgate, 2002).

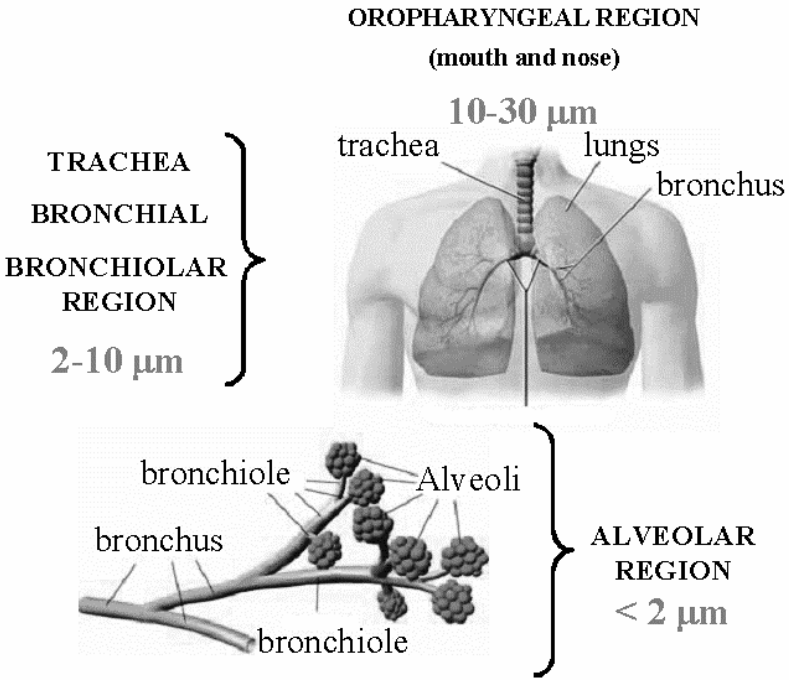


Figure 2.4 Deposition of particles within human respiratory system. Illustration indicates the depth of particles deposition according to their aerodynamic diameters; the smaller the particles the deeper the penetration (Weitz, 2009).

There are different types of particles which can have different harmful effects on human health. As the evidence suggests that risks to human health associated with exposure to anthropogenic particulate matter are higher than risks associated with exposure to naturally occurring particles in ambient air, the EU developed the **regulatory classification system** which set the definitions for PM_{10} (referred in page 13) and for $PM_{2.5}$ (EU Directive, 1999) as:

- $PM_{2.5}$ is particulate matter which passes through a size selective inlet with a 50% efficiency cut-off at 2.5 μm aerodynamic diameter.

The selection of PM_{10} as an indicator was based on health considerations and was intended to focus regulatory concern on those particles small enough to enter the thoracic region, whereas the use of $PM_{2.5}$ standard was based primarily on epidemiological studies (Wilson et al., 2002).

Nowadays, many authors misuse the original terms based on considerations of size-selective sampling. A great inconsistency can be also found on using the terms “inhalable”, “thoracic” and “respirable”. Therefore, the meaning of each term, unless defined, must be interpreted from usage of author. To avoid any misunderstanding, for the purposes of this work the following terms are used:

- PM_{10} corresponds to particulate matter which passes through a size-selective inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter.
- $PM_{2.5}$ corresponds to particulate matter which passes through a size selective inlet with a 50% efficiency cut-off at 2.5 μm aerodynamic diameter (fine fraction).
- $PM_{2.5-10}$ corresponds to PM_{10} without $PM_{2.5}$ (coarse fraction).

2.4 Sources of particulate matter

In general, particulate matter is originated from a wide range of natural and anthropogenic sources. Particles from both these sources are further divided into two groups, namely primary and secondary. Literally, primary particles are originated directly from their sources while secondary particles are formed within the atmosphere from condensation of vapours, or as a result of chemical reactions. Primary aerosols are usually of natural origin whereas secondary ones are predominately of anthropogenic origin (Buringh and Opperhuitzen, 2002).

The natural sources of particulate matter include soil and volcanic dust, sea salt spray, sand and dust from wind storms, pollens, spores, bacteria, plant fibbers, and etc. Soil dust is considered to be the largest natural source of particles worldwide (Holgate et al., 1999), the evaporation of sea water being very important especially for coastal areas. The particles from these sources are mainly of bigger sizes and they significantly contribute to PM_{10}. In Portugal the largest natural sources are:

- sea salt sprays;
- forest fires;
- Sahara desert particles due to their long-distance transport.

There is a wide range of anthropogenic sources of PM such as the use of fossil fuels for heating, transportation, industry and energy conversions (Godish, 1991). The incinerations of municipal and private wastes also contribute to the particulate pollution of atmosphere as well as handling and processing operations of various industries. The great number of these sources led to further divisions. PM is originated either from mobile sources that include various types of transportations (motor vehicles, aircraft, railroads) or from stationary sources, i.e. residential and industrial power plants, industrial processes, and solid waste disposals.

In Europe the majority of PM is originated from anthropogenic sources, mainly from industrial fossil fuel combustion (29% and 32% for PM_{10} and $PM_{2.5}$, respectively) and from production processes (14% for PM_{10} and 15% for $PM_{2.5}$). On average, the road transport represents the second most important source of PM in EU with 17% and 20% for PM_{10} and $PM_{2.5}$, respectively (Holgate et al., 1999), but in some places traffic emissions are the most important source of air pollution (Harrison et al., 1997). Due to the general improvements and better controlled technologies, EU traffic PM_{10} emissions were reduced between 1990 and 2006, contributing 17% of the total EU reduction of PM emissions (EEA, 2008). Despite these decreases the Member States of European Union have still difficulty to fulfil the legislative ceilings of traffic related pollutants (EEA, 2008A), mainly due to the fact that the demand for road transport has been growing much faster than it was anticipated (EEA, 2008B). Another recent report of European Environment Agency (EEA) has confirmed that traffic emissions (i.e. emissions from road transport) has remained the main source of health-damaging pollutants, being the most significant source of nitrogen oxides, carbon oxide, and the second most important source of PM_{10} and $PM_{2.5}$ (EEA, 2008C); in urban areas traffic emissions are the major contributor of atmospheric particles, increasing greatly both PM_{10} and $PM_{2.5}$ (Heinrich et al., 2005). Furthermore, the particle size distribution of emissions from vehicle exhausts showed that the respective particles belong mainly to $PM_{2.5}$ fraction (Holgate et al., 1999A).

In Portugal total PM emissions in year 2006 were 140 Gg and 111 Gg for PM_{10} and $PM_{2.5}$, respectively (EEA, 2008C). Regarding the traffic PM (i.e. specifically associated with road transport), the emissions were 7.0 Gg for both PM fractions, and these amounts represented, respectively, 2% and 3% of the EU traffic PM_{10} and $PM_{2.5}$ (EEA, 2008C).Out of 27 EU Member States, Portugal was, respectively, the 12-14th and the 8-11th largest contributor of traffic PM_{10} and $PM_{2.5}$. It is especially alarming though that contrary to the other EU countries

where traffic PM decreased during last two decades, in Portugal PM_{10} and $PM_{2.5}$ from traffic emissions increased by 18% between 1990 and 2006 (EEA, 2008C). This information indicates that traffic PM in Portugal is a matter of great concern and the reduction of these emissions, mainly related to the $PM_{2.5}$, is fundamental in order to protect public health.

2.5 Chemical composition of particulate matter

2.5.1 General composition

Chemical composition of particulate matter is a very complex topic. Up to this date it has been suggested that there is a close relationship between particle size, shape and chemical composition. For example, a particle from metallurgical industries composed of heavy metals tends to have rounded shape due to the condensation of these metals. Certainly, there is also a relationship between particle origin and its chemical characteristics. Still, even particles from the same type of source may vary in their chemical (and physical) compositions due to different conditions, such as different source location, different time or different emission rates.

The importance of the chemical characterisation of PM has become known recently when some studies pointed out that chemical composition of PM significantly contribute to PM adverse health effects (Harrison and Yin, 2000). The presence of some toxic compounds such as heavy metals and polycyclic aromatic hydrocarbons in PM can cause eventually more adverse effects for human health. Consequently, more detailed characterisation of particulate matter originated mainly from anthropogenic sources (traffic and industrial emissions), which is most likely to contain these toxic substances, became of a great importance.

In general particulate matter consists of the following (Holgate et al., 1999A):

- inorganic water soluble material;
- inorganic water insoluble material;
- carbonaceous material.

Inorganic water soluble material may represents on average between 25-35% of PM. This material can be further divided into chemical groups that may include sulfates, nitrates, and

chlorides, being widely combined with ammonium and cations of sodium, calcium, and magnesium (Seinfeld and Pandis, 1998). In sea salt, typically sodium is present with chlorides while calcium occurs primarily in sulfates; magnesium can occur with chlorides in close vicinity to sea (Maynard and Howard, 1999).

Inorganic water insoluble material accounts for approximately 20% of PM. It includes various minerals such as quartz, calcite, gypsum, or montmorillonite (Holgate et al., 1999A); heavy metals are also present.

Carbonaceous material comprises approximately 40% of PM being represented by different species of carbon, as further discussed in the following chapter. An example of chemical composition of PM sample is shown in Figure 2.5.

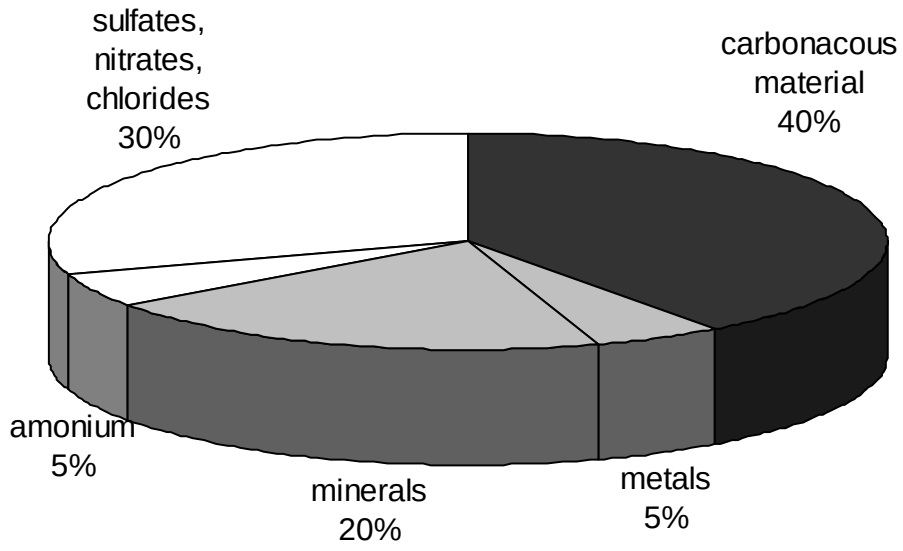


Figure 2.5 An example of general chemical composition of PM (Holgate et al., 1999A).

Although there is no general rule, it seems that some chemical species can be more associated with $PM_{2.5}$, including heavy metals (Spurny, 1999A) or carbonaceous species (Table 2.1). $PM_{2.5-10}$ fraction is more attributed with minerals from dust and sea salt, but some anthropogenic species were also found in this fraction, although in much smaller proportions (Maenhaut et al., 1996).

Table 2.1 Examples of chemical composition (%) of PM_{10} and $PM_{2.5}$ at rural, urban background, and traffic sites (Krzyzanowski et al., 2005)

Component	PM_{10}			$PM_{2.5}$		
	Rural	Urban background	Traffic	Rural	Urban background	Traffic
Organic carbon	16	20	22	23	22	29
Elemental carbon	6	5	13	8	8	17
Minerals	10	9	19	5	7	8
Nitrates, sulfates	32	35	24	42	43	30
Sea salt	8	4	3	3	3	1
Other	28	27	19	19	17	15

2.5.2 Metals

The characterisation and quantification of metals in PM were brought to the scientific attention because of the health issues they raise.

Almost all metals that occur in the atmosphere are associated with particles. Some metals in airborne particles are of natural origin, i.e. from volcanic dust, oceanic aerosols, and soil crust (Schroeder et al., 1987). Depending on the composition of the local geological formation, soil crust may include metals such as iron, manganese, zinc, lead, vanadium, chromium, nickel, cobalt, copper, arsenic, lead, cadmium, and antimony (in order of descending abundance); in the north of Portugal aluminium and potassium are highly associated with soil crust (Begonha, 1997). Nevertheless, the majority of metals found in PM are originated from various anthropogenic sources, such as high temperature industrial processes, waste incinerations, power plants, and traffic emissions from motor vehicles, being usually present in $PM_{2.5}$ (Holgate et al., 1999A).

Regarding the traffic emissions, previous research has mostly focused on metals in particles from vehicle exhausts, because it was generally assumed that fuel combustion is the primary mechanism by which they are formed. However, other non-exhaust sources such as pavement abrasions, road dust, tyre and vehicular part abrasions also contribute to these emissions (Sagebiel et al., 1997; Kleeman et al., 2000). In urban environments and traffic locations especially brake and tyre wear are an important source of metals in traffic related PM (Thorpe and Harrison, 2008).

Up to this date a wide range of metals was identified in PM emitted from brake and tyre abrasions, including arsenic, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead, and antimony, as shown in a review given by Thorpe and Harrison (2008). Although these authors provided an extensive summary on non-exhaust PM emissions, they concluded that with exception of brake particles that can be identified from their copper or antimony content, unequivocal identification of particles from other non-exhaust sources will prove to be difficult due to lack of suitable trace metals and because of the interaction between sources prior to the emission process. As the understanding of metal emissions generated by non-exhaust sources is far from comprehensive, it is currently appropriate to determine particulate metal content as total that represents for each metal the sum of all species emitted from various traffic-related sources.

Particulate metals can be found in a great variety of different compounds, being also present in both soluble and insoluble elemental state (Holgate et al., 1999B), but mostly in low concentrations. Due to these low concentrations the analyses of metals in airborne particles tend to be difficult. Although some techniques such as proton induced X-ray emission analysis have overcome the limitations that are associated with quantification of metals in PM, they provide information on the total metal content rather than specific compounds and chemical species. They also do not give information concerning the composition of particles according to their specific shapes and sizes. Such information can be obtained through scanning electron microscopy (SEM) combined with X-ray microanalysis by energy dispersion spectrometry (EDS), providing detailed information on the size and morphology of individual particles as well as on the composition (Casuccio et al., 2004; Xie et al., 2004). Therefore to study the particulate metal content an optimal solution might be to employ various analytical techniques including SEM-EDS. Nevertheless, this approach, although very thorough, may prove to be financially and time consuming, because for SEM-EDS a great number of individual particles must be analysed to obtain a representative sample.

2.5.3 Carbonaceous species

Carbon is seemingly an important, if not the most important, constituent of particulate matter in Europe (Kubatova et al., 1999; Krivacsy et al., 2001; Putaud et al., 2004). In airborne particles carbon can be present in three different forms, which include inorganic carbon, organic carbon and elemental carbon. Assuming that inorganic carbon content in PM is

negligible (Sharma et al., 2005) the sum of organic and elemental carbon then represents the total carbon content.

Elemental carbon results from incomplete combustion of coal, biomaterial and fuels (transport section); in urban areas and in close proximity to major roadways, traffic is the major contributor (Pakkanen et al., 2000; Viidanoja et al., 2002). Elemental carbon is non-volatile and its chemical transformations are limited, therefore, it is a good indicator of primary anthropogenic air pollutants (Ho et al., 2002; Kim et al., 2000). Its content in PM varies, usually elemental carbon represents between 5 and 40% of PM mass (Spurny, 1999B), depending on the particle origin. The surface area of particles with elemental carbon is greatly increased by their porous surface, thus significantly increasing their ability to receive more airborne chemical substances; particles with elemental carbon are carriers for organic compounds, heavy metals and soluble inorganic material.

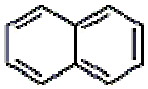
Organic carbon represents thousands of different carbon containing compounds, such as n-alkanes, n-alkanoic acids, polycyclic aromatic hydrocarbons, alcohols, alkanones and others (Brown et al., 2002). These compounds can be volatile, semi-volatile, and non-volatile, a characteristic that is closely associated with molecular weight of the compounds and which influences the behaviour of the compounds in relation with particles. Low molecular weight organic compounds are usually volatile remaining in the atmosphere in gaseous form. As their molecular weights increase they tend to condensate at the surfaces of particles being then accounted as carbon aerosol. Semi-volatile organic compounds are present in both gaseous form and adsorbed (or absorbed) on the particles; non-volatile compounds are associated with particles (Holgate et al., 1999A). Organic carbon can either be emitted directly from primary emission sources that include various combustion processes (vehicles, power plants, coal and wood burning), or it can be generated by chemical reactions among primary gaseous organic carbon species in the atmosphere (Kim et al., 1999; Lonati et al., 2005). The relative contributions of primary versus secondary emissions of organic carbon depend on the types of local emissions, meteorology and atmospheric chemical conditions. The content of organic carbon in PM varies greatly. In the polluted urban areas of Europe, organic carbon contributes to approximately 20% of PM_{10} and 30% of $PM_{2.5}$ (Krzyzanowski et al., 2005); in remote areas it is reported that organic carbon contributes to approximately 16 and 10% of $PM_{2.5}$ and $PM_{2.5-10}$, respectively (Putaud et al., 2004).

A great deal of research during past years has been focused on the relationship between carbonaceous species and PM from vehicle traffic. It was observed that in urban areas and in vicinities of highways and major roads, traffic emissions contribute to a large part of both organic and elemental carbon, being especially important for $PM_{2.5}$ (Pakkanen et al., 2000; Ruellan and Cachier, 2001; Viidanoja et al., 2002). Still, to fully understand the fate of traffic related PM in Europe and their effects on public health, more research is required. It is important to continue measuring carbonaceous species in PM at both polluted and background areas and to compare their characteristics, special attention being focused on $PM_{2.5}$.

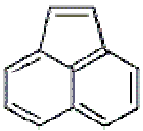
2.5.4 Polycyclic aromatic hydrocarbons

A major reason to study the organic content of particulate matter is that organic compounds present in PM pose hazards to human health. In that regard polycyclic aromatic hydrocarbons (PAHs) are one of the most important compounds, being a large group of organic compounds with two or more fused aromatic rings (Figure 2.6). They are originated from a wide variety of natural and anthropogenic sources, being generally produced during incomplete combustion of organic matter such as coal, oil and gas (Shibamoto, 1998). PAHs in the urban atmosphere are mainly of anthropogenic origin; road traffic is one of the most important anthropogenic emission sources, in urban areas contributing by as much as 74% (Omar et al., 2002). Industrial processes and burning of domestic fuels are also significant sources of PAHs (WHO, 1998). The increasing amount of aircrafts and associated emissions in recent years could also contribute to atmospheric concentrations of PAHs. Although the role of these potential sources could be important for levels of PAHs in air, they have never been surveyed in this regards anywhere in the world yet.

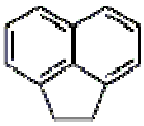
In general, PAHs are ubiquitous compounds with low solubility in water, high melting and boiling points, and low vapour pressures. While the physical-chemical properties of PAHs vary considerably, the semi-volatile properties of some PAHs make them highly mobile throughout the environment, with deposition and re-volatilisation processes distributing them between air, soil and water; some PAHs are subject to long-range transport through the atmosphere making them a transboundary environmental problem. PAHs, whether dissolved in water or present in the air, can undergo photodecomposition in the presence of the ultra violet light from solar radiation (Park et al., 2002).



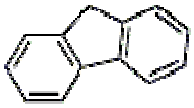
Naphthalene



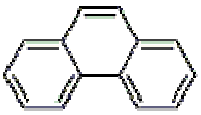
Acenaphthylene



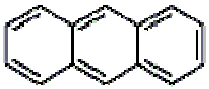
Acenaphthene



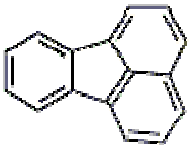
Fluorene



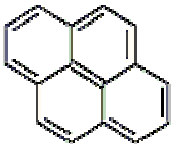
Phenanthrene



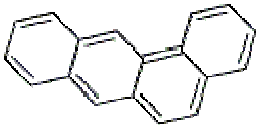
Anthracene



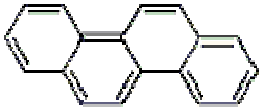
Fluoranthene



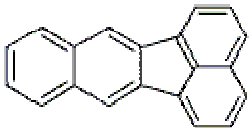
Pyrene



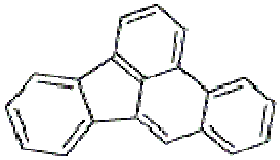
Benz[a]anthracene



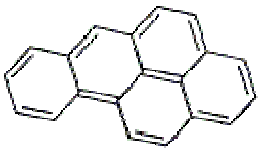
Chrysene



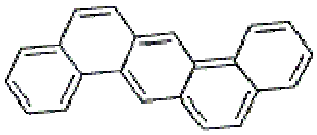
Benzo[b]fluoranthene



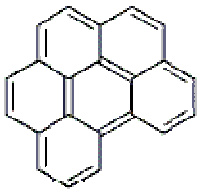
Benzo[k]fluoranthene



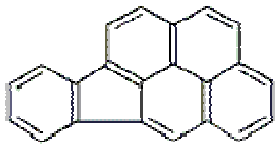
Benzo[a]pyrene



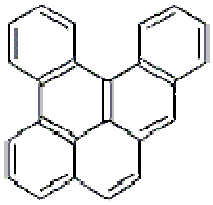
Dibenz[a,h]anthracene



Benzo[ghi]perylene



Indeno[1,2,3-cd]pyrene



Dibenzo[a,l]pyrene

Figure 2.6 Molecular structures of 16 PAHs listed as priority pollutants by U.S. Environmental Protection Agency (USEPA) and of dibenzo[a,l]pyrene (Shibamoto, 1998).

In the ambient air PAHs are present both in the vapour phase as well as bound to the particulate matter. PAHs with low molecular weight are usually found more in the vapour

phase, while PAHs with four or more rings are found mainly in the particle phase (Srogi, 2007). Especially these particle-bound PAHs are the most harmful to humans (Section 2.6.3), among those benzo[a]pyrene being one of the mostly studied compound; its annual mean concentrations in ambient air greatly vary, being between 0.1 and 1 ng m^{-3} at the rural sites, between 0.5 to 5 ng m^{-3} at the urban sites, and reaching up to tens of ng m^{-3} in the direct vicinity of the industrial installations.

2.6 Health effects

2.6.1 Particulate matter

During the last three decades PM has been extensively studied within many epidemiological studies. In North America some studies showed that people living in cities with **long-term** exposure to higher PM_{10} and $PM_{2.5}$ concentrations died earlier than those living in cities with lower air particulate pollution (Dockery and Pope 1994; Pope et al., 1995). These studies raised much of public concern because of their implication on public health. The epidemiologists found out that the number of deaths related to PM_{10} in these two studies were significantly higher than those previously known from times-series (i.e. short-term) studies, because these studies only detected deaths related to air particulate pollution in days or weeks after the pollution event (Kunzli et al., 2001), omitting the deaths associated with chronic exposures.

As far as it is known, in Europe there have been no studies evaluating the relationship between long-term exposure to increased PM_{10} and $PM_{2.5}$ concentrations and mortality. More information have been reported regarding the health impact assessment of long-term exposure to PM_{10} on lung function and chronic respiratory syndromes mostly in children (Horak et al., 2002; Janssen et al., 2003); it was estimated that long-term exposure to a 10 μg m^{-3} increase in PM_{10} concentrations led approximately to an increase of 10% in bronchitis in adults and 31% in children (Kunzli et al., 2000).

Since the episode of air pollution in London in 1952, many studies have reported that **short-term** exposure to increased PM also lead to increased mortality rates (Katsouyanni et al., 1997). Furthermore, it have been concluded (WHO, 2000A) that there is not any threshold below which the relationship between PM_{10}, $PM_{2.5}$ and mortality will not have any effect. The

lack of a threshold implies there is no safe level of PM concentrations at which a guideline can be set, thus an adequate judgment has to be made concerning this subject.

With increasing PM_{10} concentrations hospital admissions for respiratory and cardiovascular diseases also increased (Atkinson et al., 1999; Atkinson et al., 2001); it was reported that a 100 μg m^{-3} increase of PM_{10} concentrations led to 10-12% increase of hospital admissions related to asthma and chronic pulmonary diseases (Katsouyanni et al., 2001). The exposure to particulate pollution may also lead to a number of other adverse health effects, such as increasing respiratory symptoms, cough, sore throat, cardiac arrhythmias and others (Kunzli et al., 2000). Evaluating more specific health outcomes, it was shown that increases of PM_{10} concentrations had significant pertinence on other lung disorders (such as wheeze and shortness of breath), on reduction of lung functions and on cardiovascular diseases, while $PM_{2.5}$ were strongly associated with cardiopulmonary diseases and lung cancer (Gemenetzis et al., 2006). Although the discussion among the scientific community continues, it is now generally accepted that particulate pollution has acute effects on mortality and morbidity rates, namely on cardiovascular and pulmonary diseases. However, the mechanisms of all these health effects are not well understood yet. It is very likely though that the adverse health effects are influenced by particle characteristics, the size of particle being the most important parameter responsible for these effects, as it determines the place of particle deposition in respiratory tract. Upon inhalation PM_{10} and $PM_{2.5}$ are deposited on the wall of airways and lungs; the smaller the particles the deeper the penetration within the system (Kaiser, 2000). While larger particles deposit mainly in the nose and throat, particles of $PM_{2.5}$ penetrate in the deeper parts of the lungs, being able to reach the alveoli. Therefore, the attention has been recently focused on $PM_{2.5}$ (WHO, 2006) and consequently it was concluded (Pope et al., 2002) that especially this fraction of PM_{10} is associated with some of the more serious health effects (mortality, lung cancer). Nevertheless, as it has been lately shown, other PM properties such as chemical composition also significantly contribute to PM adverse health effects (Harrison and Yin, 2000), suggesting that they are the result of a complex (eventually synergic) interaction of multiple particles properties with the respiratory tract. Obviously, further understanding of PM is necessary to design effective air pollution strategies, for appropriate reduction of risks associated with air particulate pollution.

Recently, some short-term exposure studies also found that when PM_{10} concentrations increased by 100 μg m^{-3}, the increase of daily mortality was on average of 6% (Katsouyanni

et al., 2001). Among European cities, the increase of mortality differed significantly, and higher risks were found in cities with warmer climate and higher NO_2 concentrations; with high NO_2 concentrations the increase of mortality with PM_{10} increase by 100 μg m^{-3} was 8%, while it was 1.9% in cities with low NO_2 concentrations (Katsouyanni et al., 2001). A possible explanation of these findings might be that particles emitted by traffic are more toxic than particles emitted by other sources. Based on elemental composition some authors (Laden et al., 2000) showed that an increase of 10 μg m^{-3} in $PM_{2.5}$ concentrations from traffic emissions was associated with a 3.4% mortality increase, being three times higher than the corresponding mortality increase associated with $PM_{2.5}$ from coal combustions. In addition, it was estimated (Kunzli et al., 2000) that for some European countries (France, Switzerland and Austria, total population of 74 million inhabitants) 3% of total mortality per year (i.e. 20 000 deaths) are due to traffic emissions, and that hypothetically total omission of traffic emissions would lead to prolonged life expectancy of 0.35 years.

Hot spots of local importance concerning human exposure to traffic PM are the densely populated areas around traffic thoroughfares and footpaths (van Vliet et al., 1997; Guo et al., 1999; Janssen et al., 2001; Heinrich et al., 2005), providing evidence that effects are related to the distance from major roads or to traffic density (mainly of heavy duty traffic). A Dutch study confirmed that mortality rates were associated with exposure to traffic particles, showing that a relative risk of 1.95% was estimated for people living within the distance of 50 m to major road (or 100 m from a highway) (Hoek et al., 2002).

To make the research correctly answering the present concerns, PM needs to be addressed more specifically. The sources of PM should be addressed, especially vehicle traffic emissions, as they are one of the most important in Europe. More information about $PM_{2.5}$ should be obtained, including the detailed physical-chemical characterisation.

2.6.2 Metals

The characterisation and quantification of metals were brought to the scientific attention because of the health issues they raise. Up to this date, arsenic, cadmium, and their compounds have been considered by International Agency for Research on Cancer (IARC) as known carcinogens to humans (i.e. Group 1) (IARC, 1980; IARC, 1990; IARC, 1993). The compounds with chromium (VI) and nickel have also been considered as carcinogenic to

humans, whereas inorganic lead compounds are probable carcinogens (Group 2A) (IARC, 1996); cobalt and it compounds have been considered as possible carcinogens (Group 2B) (IARC, 2006).

Other metals, such as manganese, cobalt, vanadium, iron, antimony, and copper also pose serious risks to humans, causing severe health effects to lungs, kidneys, livers, skin, heart, and to digestive system (Holgate et al., 1999C).

Regarding the metals in PM, the epidemiological evidence is far from being comprehensive. Some studies have suggested that close to the steel mills the transition particulate metals could be important (Beckett, 2001; Ghio and Devlin, 2001), as they are possible significant components concerning PM-induce cardiovascular effects and they potentiate the inflammatory effects of particles (Costa and Dreher, 1997; Wilson et al., 2002A). Nevertheless, metal quantities associated with PM of most environments are smaller, and it has not been established yet that those quantities are sufficient to cause adverse health effects. Some of the studies have addressed the role of specific metal particles, and it seems that iron, zinc, nickel, copper and vanadium might be especially important (WHO, 2003).

Concerning the respiratory system, it has been shown that lung injuries occurred after the exposure to metal particles (Holgate et al., 1999C). In particular, water soluble metals such as zinc and copper were found to induce various lung injuries and inflammation (Prieditis and Adamson, 2002; Dreher et al., 1997).

2.6.3 Polycyclic aromatic hydrocarbons

The individual PAHs are extremely hazardous to human health. Many of them are cytotoxic and mutagenic (WHO, 1998) being the largest known group of carcinogens. The carcinogenic potency of individual PAHs is widely varying. Out of the sixteen PAHs listed by USEPA as priority pollutants benzo[a]pyrene has been classified as known carcinogen to humans (IARC, 1983), whereas other PAHs have been considered as probable (Group 2A) and possible (Group 2B) human carcinogens (IARC, 1983; IARC 2002). Table 2.2 shows the carcinogenicity of 16 USEPA PAHs and dibenzo[a,l]pyrene using different classification systems of IARC, USEPA and the concept of Toxicity Equivalency Factor (TEF) that estimates carcinogenicity relatively to benzo[a]pyrene.

Table 2.2 Classification of PAH carcinogenicity

Compound	Classification		
	IARC[a]	USEPA[b]	TEF[c]
Naphthalene	2B	C	not available
Acenaphthylene	not available	D	0.001
Acenaphthene	3	not available	0.001
Fluorene	3	D	0.001
Phenanthrene	3	D	0.001
Anthracene	3	D	0.01
Fluoranthene	3	D	0.001
Pyrene	3	D	0.001
Benz[a]anthracene	3	B_2	0.1
Chrysene	2B	B_2	0.1
Benzo[b]fluoranthene	2B	B_2	0.1
Benzo[k]fluoranthene	2B	B_2	0.1
Benzo[a]pyrene	1	B_2	1
Dibenz[a,h]anthracene	2A	B_2	5
Benzo[ghi]perylene	3	D	0.01
Indeno[1,2,3-cd]pyrene	2B	B_2	0.1
Dibenzo[a,l]pyrene	2A	not available	100[d]

[a](IARC, 1983; IARC, 2002; IARC, 2009A): Group 1 - carcinogenic to humans; Group 2A - probably carcinogenic to humans; Group 2B - possible carcinogenic to humans; Group 3 - unclassifiable as to carcinogenetic in humans; Group 4 - probably not carcinogenic to humans.

[b](USEPA, 1986): Group A - human carcinogens; Group B - probable human carcinogens (B_1: based on limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in animals; B_2: based on sufficient evidence of carcinogenicity in animals); Group C - possible human carcinogens; Group D - not classifiable as to human carcinogenicity; Group E - evidence of non-carcinogenicity for humans.

[c]Toxicity Equivalency Factor (TEF): estimation based on the relative potency to benzo(a)pyrene (Nisbet and LaGoy, 1992).

[d](Pufulete et al., 2004)

PAHs are typically found in a mixture of many compounds. In studies that estimate human cancer risk from exposure to complex mixtures of PAHs, benzo[a]pyrene has been commonly used as a substitute for other PAHs in these mixtures, due to its strong carcinogenicity, assuming that its contribution to carcinogenic potency of most environmental PAH mixtures is generally constant. However, appropriateness of this approach has been lately questioned. The concerns are related to the variability of the compositions of different PAH mixtures. For example benzo[a]pyrene represents only 4% of the total PAHs in most particles originated from combustions. In various mixtures, low-potency PAHs such as fluoranthene may occur in high concentrations or, as recently discovered, some PAH compounds could be present in minor amounts, nevertheless possessing higher carcinogenic potency (such as dibenzo[a,l]pyrene with potency two orders of magnitude higher than benzo[a]pyrene). To solve the mentioned problems, another approach to estimate the human cancer risk from exposure to complex PAHs has been proposed using TEF concept. The use of the TEF of each compound in PAH mixture allows to set the sum of all concentrations, weighted for their carcinogenetic potency relative to that of benzo[a]pyrene. It is important to point out though that the present studies, which evaluate the toxic effects of PAH mixtures, do not recognise the interactions between the individual PAH compounds in mixtures, which can result in significant increases of health risks. At this moment the complete understanding of these interactions is not possible as the current knowledge is still limited, thus these problems are yet to be solved by the scientific community.

Because of their toxic, mutagenic and carcinogenic properties there has been widespread interest on analyzing and evaluating the exposure of humans to PAHs in ambient air. Nevertheless, for the obvious reasons, up to this date there are no studies in which the humans were deliberately exposed to PAHs. The information on the effects of inhaled PAHs comes only from epidemiological biomarker studies of humans exposed to PAHs in work places or in urban environments. Such studies were conducted in northern region of Czech Republic considering people living in the heavily polluted area of Teplice city, with ambient concentrations of benzo[a]pyrene up to tens of ng m^{-3} (Sram et al., 1996; Dejmek et al., 2000). Also considering Teplice city Binkova et al. (1996) studied the effect of personal

exposure to carcinogenic PAHs on DNA adducts*, comparing women working as postal workers with those living in the low-polluted district of Prachatice. They found a significant correlation between individual exposures to carcinogenic PAHs and DNA adducts, this effect being significant especially for non-smokers (Binkova et al., 1995). Other studies were performed in less polluted areas (concentrations of benzo[a]pyrene lower then 5 ng m^{-3}) such as Copenhagen, Florence and Prague (Nielsen et al., 1996; Palli et al., 2001; Novotna et al., 2007), considering bus and taxi drivers and policemen, extensively exposed to PAHs. Although the results of these studies were not completely consistent, they indicated that exposure to levels of PAHs present in urban air, even at relatively low concentrations, resulted in increased levels of various biomarkers specific for PAHs.

The health concerns of PAHs have been traditionally focused on their potential carcinogenicity in humans, which seems to be beyond dispute. PAHs are genotoxic compounds and their carcinogenicity is probably mediated by their ability to damage the DNA (Novotna et al., 2007). Even exposure to low doses of PAHs might be associated with various cancers, indicating that there is no safe threshold. However, regarding the PAH carcinogenicity due to exposure to polluted air, it is important to point out that there is no epidemiological evidence showing that at levels present in urban air PAHs cause cancer. Until now the only evidence of PAH carcinogenicity in humans exists for long-term exposure (of many years) to polluted air of work places with high concentrations of PAHs, which exceed those in ambient air by orders of magnitude (Peluso et al., 2001; Bostrom et al., 2002). Clearly, the carcinogenicity of PAHs stills raises many questions, mainly related to air pollution exposure. Due to the lack of useful, good-quality data, the quantitative cancer risk estimates of PAHs as air pollutants are very uncertain, because they are based on extrapolation from substantially higher occupational concentrations, which makes difficult to draw conclusions (Bostrom et al., 2002). Furthermore humans are never exposed only to a single PAH compound in ambient air, and the coexistence of PAHs in various mixtures implies further difficulties. To fully understand the carcinogenesis of PAHs and their role as air pollutants, these issues need to be correctly addressed by further research.

*DNA adducts represent a reliable biological marker widely used to identify health hazards and to evaluate the dose-response relationship in humans exposed to carcinogens and to mutagenic compounds (Peluso et al., 2001)

Recently, several studies have also suggested that exposure to PAHs in ambient air may have other effects than cancer. Foetuses in particular are highly susceptible to the exposure of PAHs because of their physiologic immaturity (Sram et al., 1999). As their developing organ systems are more vulnerable to these pollutants, prenatal exposure to environmental PAH pollution may results in some adverse birth outcomes (Perera et al., 1998; Perera et al., 2003; Vassilev et al., 2001). Nevertheless, the mechanisms of these outcomes are not well understood yet.

Most of the carcinogenic PAHs present in ambient air are found adsorbed on the particles, therefore the interest of the present research has been focused on carcinogenicity of ambient air particles and in particular on the role of PAHs. Recent studies (Ma and Ma, 2002; Nel et al., 2001) indicate that ambient PAHs bound to particles can play a role in the inflammation induction, contributing to carcinogenicity as well as to worsening of respiratory and cardiovascular diseases. However, these issues need to be further addressed, until now it was not possible to distinguish between the toxic effects of airborne PAHs alone or in combination with particles to which they are bound to.

2.7 Indoor air

As people spend 80-90% of their time indoors the quality of indoor air is an important (if not the most important) factor influencing human heath. It is a common belief that being indoors, one is safe from harmful pollutants. Sadly, this is not true, as the scientific evidence has shown that indoor air at homes can be more seriously polluted than outdoor air of the largest and most industrialised cities. Furthermore, people who constantly stay indoors, thus being chronically exposed to indoor pollution, are often those most susceptible ones (infants, children and seniors). To understand the relationship between indoor air quality and health, it is important to further study the indoor pollutants that have the most hazardous effects on human health, particulate matter being one of the priority pollutants.

2.7.1 Historical overview

Indoor air pollution has much longer history than it is usually thought, as some archaeological evidence suggests that indoor pollution was widely experienced in distant past. Mummified lung tissues, preserved by tanning, freezing or desiccation, proved to be most useful to

provide information on prehistoric exposure to particulate matter. The samples of these tissues can be re-hydrated, allowing subsequent microscopic examination to identify solid materials deposited in the lungs. Up to this date, various materials (mineral and wind-blown dust) that caused pneumoconiosis and silicosis were identified in samples of lung tissues throughout many different epochs and geographical locations (i.e. from a mummy of ancient Egypt, from Peruvian miner of sixteenth century, from East Anglian flint-knappers) (Holgate et al., 1999C); the most frequent occurrence was found for anthracotic particles being a result of lifelong exposure to smoke indoors.

The smoke was certainly the major source of pollution indoors being especially associated with particles. The first human habitations were poorly ventilated and the use of open fires probably led to high levels of indoor pollution. Perhaps even then, people were able to recognise intuitively the adverse effects associated with exposure to particles, as in Romano-British Period, cooking was done outdoors or away from living areas. Nevertheless, during Dark Age the huts still did not have chimneys and the smoke from the central hearth simply rose and then slowly escaped through holes in the roof; in such conditions high levels of particles were present. Thus, the use of chimneys in early modern period was a particularly relevant technological change which improved the indoor air quality. By the Elizabethan time chimneys became far more common and effective, and thus widely used. It is important to point out that these transformations were accomplished with some scepticism and prejudice; indoor smoke was considered important in hardening the timbers of the house and warding off the diseases among its habitants (Holgate et al., 1999C). Perhaps it was the reason why stoves, another step of technological development, never really took hold in England although some attempts were made; stoves grew especially popular on the continent significantly reducing exposure to indoor smoke.

Since the beginning of the twentieth century, there has been an increased interest regarding the indoor air. Especially during the last two decades public attention has been focused on the risks associated with poor indoor air quality. The exposure levels to harmful indoor air pollutants, such as PM, have been increasingly considered for the protection of human health. To assess those exposure levels, evaluation of the concentrations and distributions of indoor contaminants, potentially toxic and/or carcinogenic, is a matter of major importance.

2.7.2 Indoor PM sources

Indoor particles originate from many different sources, such as combustion sources (gas, coal, wood), cooking activities, building materials, carpets, products for household cleaning and maintenance, indoor activities (cleaning, dusting, carpet vacuuming, personal care), hobbies, central heating and cooling systems. Among these sources tobacco smoke is considered to be one of the greatest contributors of indoor breathable particles (WHO, 2000B).

Due to a variety of particle sources, the concentrations of indoor PM differ significantly among places and over times. A substantial part of indoor particles also results from outdoors. Thus, the actual concentrations of particles indoors are results of both indoor and outdoor sources, but also of other parameters such as building architecture, furniture position, etc. Undoubtedly, the "individuality" of each indoor environment implies further research difficulties for complete understanding of indoor particulate pollution and its sources.

2.7.3 Tobacco smoke

Tobacco has been smoked for centuries by the native population of China and America. It was introduced to Europe in 1492 when Christopher Columbus returned from his discovery voyage from America; after that it spread around the world. Nowadays, it is estimated that there are $1.1x10^9$ smokers throughout the world (IARC, 2004). Originally little was known about the harmful health effect of tobacco smoke, and it was used as medicine for ailments such as toothaches, worms or migraines. By the twentieth century the harmful effects of smoking have been widely recognised.

When smoking, air is drawn into a cigarette during each puff and combustion takes place forming the tobacco mainstream smoke. These emissions are inhaled by smoker; burn temperature is up to 1000 °C (Colls, 1997). Although serious pollutants such as N-nitrosamines are formed, they influence only the smoker. Between the puffs, the cigarette smoulders, and from its lit end it forms the sidestream tobacco smoke. Although the combustion temperature is lower, being approximately around 400 °C (Colls, 1997), it can lead to formation of more toxic compounds than in mainstream smoke. Furthermore, before they are diluted by air turbulences, the concentrations of toxicants in the sidestream smoke are extremely high. Environmental tobacco smoke (ETS) (also called second-handed tobacco smoke) is then the mixture of smoke present in room, consisting of mainstream smoke

exhaled into environment and sidestream smoke, after dilution and aging (Thielen et al., 2008). The aging can last for minutes or hours, but during that time the composition of all pollutants, including tobacco particles is changing.

In general, both mainstream and sidestream of tobacco smoke are very complex mixtures of gaseous phase and particles of different sizes, composed of various classes of chemical compounds. Over 4000 different chemicals were found in tobacco smoke, 50 of them being known or suspected carcinogens and more than 100 being considered chemical poisons (Colls, 1997). Some of the chemicals, such as carbon monoxide, carbon dioxide, nitric oxide, formaldehyde, and benzene are present in gaseous phase only, while others (e.g. phenol and cresols) are portioned between both phases. Carcinogenic metals, such as arsenic and cadmium, chromium, nickel, and lead (IARC, 2004; Wu et al., 1997) are mainly found in the particles, as well as tobacco-specific nitrosamines and PAHs (Thielen et al., 2008). Up today, as many as 549 PAHs were identified in tobacco smoke, twelve of them being classified by IARC as carcinogens (Rodgman and Perfetti, 2006). As most of particle components have known adverse impacts on health, the exposure to these particles represents a serious risk to human health.

Because of its effects on health, tobacco smoke has been intensively studied since the 1950s. Voluminous literature and public media linked the active tobacco smoking to lung and heart diseases and to cancers of various organ systems (Critchley and Unal, 2003). Smoking harms nearly every organ of the human body, but the full extent of the damage is still unknown. Even today, over 50 years after the first links between smoking and lung cancer were established, more diseases are being found to be caused by smoking. However, it is known that about half of all continuing regular smokers are killed by their smoking (EC, 2004); those smokers that die in middle age, lose approximately 22 years of life, with a larger proportion of that shortened life span being spent in ill health (EC, 2004). Over 3 million people are killed every year because they smoke, dying mostly due to lung cancer and aortic aneurysm (Holgate et al., 1999D); out of these over 650 000 are Europeans (EC, 2004).

Tobacco smoke affects not only people who smoke but also those who are somehow exposed to it. Undoubtedly, the exposure of smokers is much higher compared to those of non-smokers, but the smokers are voluntary exposed to tobacco smoke whereas non-smokers are not. The exposure of non-voluntary smokers cannot be underestimated as it was found that

higher levels of cancer-causing substances occurred in sidestream smoke than in mainstream smoke (Wu et al., 1997). Thus, the exposure to ETS, also called passive smoking, has also become an important health issue. Up to this date it has been proven beyond any doubt that passive smoking poses significant hazards to human health. It increases the risk and frequency of respiratory symptoms (wheeze, cough, breathlessness and phlegm) (Trude and Skorge, 2007), being a proven cause of respiratory diseases of the lower airways (croup, bronchitis, bronchiolitis, pneumonia) in childhood and probably also during adulthood (Skorge et al., 2005); extended exposure to ETS also induce various heart disease as well as lung cancer for non-smokers (EC, 2004). Thus in 1993, the USEPA classified passive smoking as a ‘‘Class A’’ human carcinogen (USEPA, 1993); accordingly, the IARC unanimously stated that exposure to ETS is carcinogenic to humans (IARC, 2004).

The concentrations of PM_{10} in ETS can reach up to 1000 $\mu g\, m^{-3}$ compared to 1-5 $\mu g\, m^{-3}$ in clean ambient air or 100 $\mu g\, m^{-3}$ in polluted ambient air; the highest concentrations can be found in poorly ventilated and crowded pubs and clubs (Colls, 1997). Recently, some European countries such as Spain or Czech Republic have recognised the risk associated with tobacco smoke, and to protect public health they ban smoking in public places. In Portugal, this legislation was set in force by January 2008 by Lei 37/2007 (Lei n.° 37, 2007). Still, passive smoking has remained an important health issue; in Western countries, with an adult smoking prevalence of 30-50%, it is estimated that over 50% of homes are occupied by at least one smoker (WHO, 2000B), resulting in a high prevalence of ETS exposure. Young children, in particular, who spend most of their time at home, are at increased risks for even greater exposures to tobacco smoke if their mothers smoke; it was estimated that ETS exposure in home increases the risk of developing asthma by 40-200% (Bernstein et al., 2008).

Although ETS is one of the most important indoor pollutants, there is still information missing, mainly related to detailed physical-chemical characteristics of respective particles. To understand the impacts of tobacco PM on public health, further studies need to be done, being focused mainly on $PM_{2.5}$.

2.8 Legislation

In May 2008 EU decided on the future of PM regulation issuing the new Directive 2008/50/EC (EU Directive, 2008). The Member States shall bring this directive in force before June 2010. Therefore, PM legislation settled in Directive 1999/30/EC (EU Directive, 1999) is still in force, being transposed to Portuguese law in April 2002 by Decreto-Lei 111/2002 (Decreto-Lei n.° 111, 2002).

2.8.1 PM_{10} regulations

The former EU Directive 1999/30/EC considered two different implementation phases for PM_{10} limits, the first one till 2005 and the second one till 2010. Concerning the 24 h mean, PM_{10} limit value was 50 $\mu g\ m^{-3}$, not being allowed more than 35 exceedances (to be obeyed till the end of first phase of implementation), and not more than 7 exceedances (to be obeyed till the end of the second phase). For annual means, two standards were set, 40 $\mu g\ m^{-3}$ to be obeyed till the end of the first phase of implementation and 20 $\mu g\ m^{-3}$ till the end of the second phase. The new Directive 2008/50/EC includes the following changes (Brunekreef and Maynard, 2008):

- the restrictions projected for the second implementation phase concerning PM_{10} limits were eliminated, showing that the level of ambition to lower exposure of European citizens to PM has been considerable lessen;

- Member States can obtain permission to postpone compliance with limit values until 2011.

Furthermore, the new directive permits larger subtraction of natural PM emissions when assessing compliance against limit values, as a stipulation that the contribution from the natural sources had to be “abnormally large” to be subtracted (Directive 1999/60/EC, article 5.4) has been lifted (article 20; Brunekreef and Maynard, 2008). In addition, the sea salt spray has been added among natural sources in the new directive (article 2.15), a change that is very important for coastal countries. As a result of these changes, higher PM concentrations are allowed.

The new directive also includes some changes regarding the position of microscale sampling points. The former directive stated that microscale traffic-oriented sampler should have been placed near to the building line (Annex VI, part II). In the new directive this has been change to no more than 10 m from the kerbside (Annex III, part C). For many EU cities, where building line is less than 10 m from kerbside, this is a relaxation of where the compliance monitoring for PM_{10} should take place. According to the new directive, the monitoring instruments may be relocated from street canyons, where the building line is closer than 10 m from kerbside, to streets where the monitors could be actually located at 10 m (Brunekreef and Maynard, 2008).

In general, all changes in the new legislation have led to reduction of the public health protection compared to the levels of protection given in EU Directive 1999/30/EC, despite the fact that the values of the PM_{10} limits themselves have not changed.

2.8.2 $PM_{2.5}$ regulations

The former Directive 1999/60/EC did not consider the $PM_{2.5}$ limits, but reflecting human health concerns, EU has recognised the importance of the subject. The new Directive 2008/50/EC promulgates $PM_{2.5}$ standards, with the aim to further reduce the adverse impacts on public health. Regarding $PM_{2.5}$, the EU has recognised that there is no identifiable threshold below which $PM_{2.5}$ would not pose risk; however, to ensure a minimum degree of public health protection, standards have been set. The $PM_{2.5}$ regulation has three major elements:

- an annual limit value;
- "an exposure concentration obligation", based on "average exposure indicator";
- a national exposure reduction target.

The new directive does not consider 24 h limit value (or target) for $PM_{2.5}$.

Concerning the annual limit value, the new directive considers two different implementation phases, the first one till 2015 and the second one till 2020, with annual $PM_{2.5}$ limits of 25 $\mu g\ m^{-3}$ and 20 $\mu g\ m^{-3}$, respectively (depending on the evidence, feasibility and outcomes of the 2013 review). At the same time, measurements of $PM_{2.5}$ at rural background sites are

recommended in order to better understand $PM_{2.5}$ impacts and to develop appropriate policies to protect public health.

The "average exposure indicator" represents the annual running mean of three consecutive years for urban background locations in zones and agglomerations throughout the territory of a Member State. The "average exposure indicator" in year 2015 should be less than 20 $\mu g\ m^{-3}$ to meet the "exposure concentration obligation".

The national exposure reduction target, which is also based on the "average exposure indicator" stipulates that with the aim of reducing harmful effects on human health, Member States should reduce their $PM_{2.5}$ concentrations by certain percentage between 2010 and 2020, depending on the level of their "average exposure indicator" in 2010. This obligation is void only when the "average exposure indicator" in 2010 is already below 8.5 $\mu g\ m^{-3}$. There is no specific rationale given for the figure of 8.5 $\mu g\ m^{-3}$; nevertheless, in studies that evaluated relationships between exposure to $PM_{2.5}$ levels and respective health responses, the concentration of 8.5 $\mu g\ m^{-3}$ represented a $PM_{2.5}$ level associated with lower risks (Pope et al., 2002; Laden al., 2000). The legislation thus recognises that $PM_{2.5}$ levels higher than 8.5 $\mu g\ m^{-3}$ are not safe, and that exposure should be in future reduced until levels well below the limit value are reached. However, the national exposure target is not legally binding as the new directive states that national exposure target will be reviewed in 2013 (article 32).

2.8.3 Carcinogenic metals and PAH regulations

Up to this date it was shown that arsenic, cadmium and nickel as well as some PAHs cause adverse health effects, being human genotoxic carcinogens. Given that the scientific community has recognised that there is a no identifiable threshold below which these compounds do not pose risk to humans, an adequate judgment has to be made to ensure the protection of public health. Thus EU has set the target values for arsenic, cadmium, nickel and polycyclic aromatic hydrocarbons in PM_{10} fraction in Directive 2004/107/EC (EU Directive, 2004). As an indicator of carcinogenic PAHs benzo[a]pyrene has been considered. The Member States were obliged to bring this directive in force by February 2007; the directive was transposed to Portuguese law in October 2007 in Decreto-Lei 351/2007 (Decreto-Lei n.° 351, 2007).

There are not any 24 h target values. For all substances mentioned previously, the directive sets the annual means of their contents in PM_{10} only (Table 2.3) being based on measurements adequately distributed along the weeks and the year (EU Directive, 2004).

Table 2.3 Target values for arsenic, cadmium, nickel and benzo[a]pyrene - set for the total content of the respective substances in PM_{10} (mean of a calendar year)

Pollutant	Target value [ng m^{-3}]
Arsenic	6
Cadmium	5
Nickel	20
Benzo[a]pyrene	1

To fully assess the contribution of benzo[a]pyrene in ambient air, EU also recommended monitoring of other relevant PAHs, such as benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene, but the target values of these compounds have not been set yet. It should be also mentioned that the suitability of benzo[a]pyrene as an indicator of carcinogenic PAHs has been recently questioned (Pufulete et al., 2004) by new findings on the presence of more potent PAHs, such as dibenzo[a,l]pyrene or dibenz[a,h]anthracene, estimated to have a carcinogenic potency approximately 100 and 5 times higher, respectively, than benzo[a]pyrene (Okona-Mensah et al., 2005).

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3. Materials and methods

3.1 Outdoor air

3.1.1 Characterisation of region

The city of Oporto is the second largest town in Portugal. It is situated in the north of the country, with approximate latitude and longitude of 41° 10' N and 8° 40' W, respectively. The city belongs to Oporto Metropolitan Area (Pereira et al., 2005) with about 1.2 million inhabitants and a population density of 540 inhabitants per square kilometre. The region is defined on the west by Atlantic Ocean with 50 km of coastline and crossed by the Douro River. This area is designated in climatic terms by North maritime, characterised by warm and dry summers and mild and wet winters with two transition seasons: spring and autumn. The zone is topographically rather uneven, with a maximum altitude of about 300 m that decreases with the coast proximity. The annual average air temperature varies between 12.5 and 15 °C, the difference between warmer and colder monthly averages being less than 10 °C. Annual air humidity is between 75 and 80% and the total annual mean precipitation is between 1000 and 1200 mm, with more than 100 days per year with precipitation equal or higher than 1.0 mm. Prevailing winds are from West and North-West. The motorisation rate is the second highest

in Portugal, and vehicle traffic is supposed to be responsible for a significant amount of the pollutants emitted to the atmosphere; previous publication showed that especially PM_{10} and ozone emissions are to be considered (Pereira et al., 2002).

3.1.2 Characterisation of monitoring sites

For the purposes of this work, the monitoring of PM_{10} and $PM_{2.5}$ was performed at four sites. Two sites were directly influenced by traffic emissions (Tr_1 and Tr_2) whereas other two sites were used for the comparison not being directly influenced by anthropogenic emissions (background Bc_1 and Bc_2).

Both sites influenced by traffic emissions were situated in Oporto in zone of Paranhos that is approximately 8 km far from the coastline, and where several public institutions, high and secondary schools as well as universities are located. The area is close to an access point of one of the most important highways connecting Lisbon and Oporto, being also the main road connection to the north of Spain. Other two major thoroughfares that encircle Oporto, providing the traffic connection within the city as well as with surrounding towns, also pass through this area; traffic emissions are the main source of atmospheric pollutants (Pereira et al., 2005). Site Tr_1 (latitude 41° 10' 39" N, longitude 8° 35' 36" W and altitude 125 m) was situated approximately 50 m west from the highway. Site Tr_2 (latitude 41° 10' 40" N, longitude 8° 35' 54" W and altitude 121 m) was located at the entrance of a car parking area (outdoor, roofless) of one of the universities, about 50 m eastwards of one of the main streets.

Site Bc_1 (latitude 41° 22' 18" N, longitude 7° 47' 27" W and altitude 1086 m) was situated in the natural park of Alvão, located in the northern interior lands of Portugal, approximately 115 km east from Oporto. Site Bc_2 (latitude 41° 48' 13" N, longitude 8° 41' 64" W and altitude 777 m) was situated approximately 15 km far from seacoast in a remote area, about 100 km north of Oporto city. There is not any significant point source in these regions and the urban agglomerations nearby should not be considered as a large pollution source. Therefore, these sites could be classified as remote ones as they fulfiled all criteria for this classification (Larssen et al., 1999). Nevertheless, as the distance from the urban agglomeration is smaller than the distance that should exist from large pollution sources, by precaution, the sites Bc_1 and Bc_2 were classified as rural (regional) background sites. The locations of all sites are shown in the Figure 3.1.

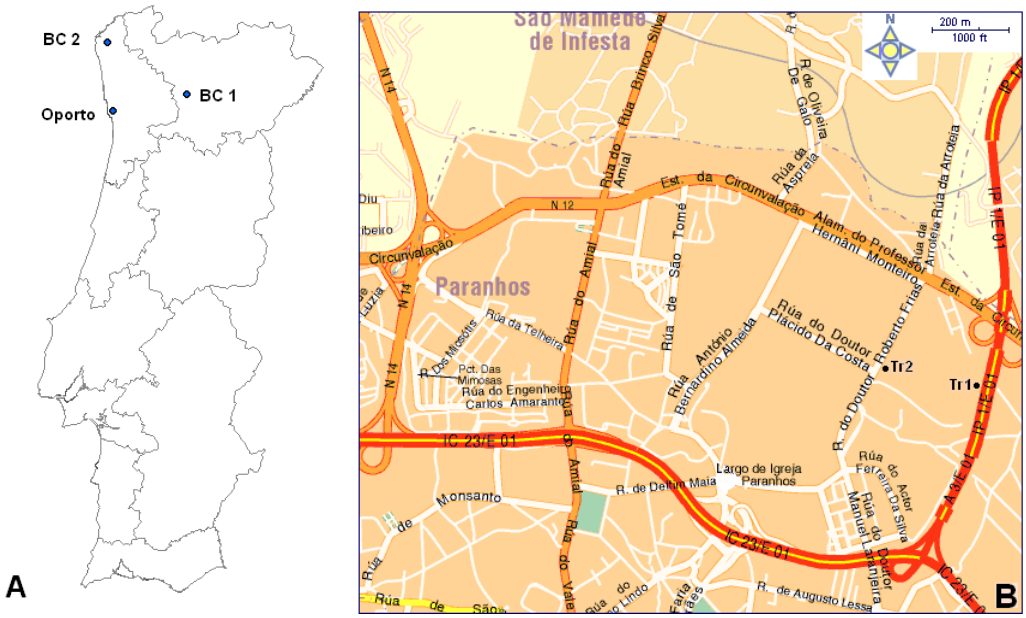

Figure 3.1 Locations of the monitoring sites: A) in Portugal, B) in Paranhos district.

3.1.3 PM sampling

The collection of the different PM fractions was done using TCR TECORA Bravo H2 constant flow samplers, combined with PM_{10} and $PM_{2.5}$ EN LVS sampling heads in compliance with the norm EN12341. A sampling air flow rate of 38.3 L min^{-1} was applied and inlets were placed 1.6 m above the ground. The monitoring equipment used to collect PM_{10} is shown in the Figure 3.2.

According to the consequent chemical analysis, different filters (∅47 mm) were used to collect PM, such as polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring (2 μm porosity) and pre-treated quartz fibre filters (900 °C for 1.5 h to remove impurities).

After the sampling the filters were kept in Petri dishes, and being covered with parafilm and aluminium foil they were appropriately stored (i.e. desiccator, fridge or freezer) for consequent chemical analysis.

Figure 3.2 PM_{10} monitoring equipment.

3.1.4 PM mass measurement

PM masses were determined gravimetrically by subtracting the initial average mass of the blank filter from the final average mass of the exposed filter; the difference was then divided by the total volume of air that passed through filter (at 25 °C and 101.3 kPa). The steps of pre- and post-sampling gravimetric mass determinations were the following: 24 h to equilibrate filters before weighing at room temperature (Mettler Toledo AG245 analytical balance with reading accuracy of 10 μg) followed by weighing during the following 24-48 h. If the measurements for one sample differed more than 50 μg, they were discarded and the filters were repeatedly weighed until three reproducible values were obtained.

3.2 Chemical characterisation

3.2.1 Bulk elemental composition

Bulk elemental composition of PM_{10} and $PM_{2.5}$ were determined by proton induced X-ray emission analysis (PIXE), a non-destructive, multi-element technique that is almost ideal for elemental analysis of suspended particles.

The PIXE technique is based on the spectral analysis of X-rays emitted from analysed matter under bombardment of the energetic ions that are most frequently charged particles (i.e. ions with no remaining electrons), such as protons. The X-rays energies are strictly determined by the atomic properties of the studied matter, and they are called characteristic X-rays. It is on these X-rays that the elemental analysis is based.

A basic PIXE setup consists of a suitable accelerator, a holder of "target" (i.e. object with the sample), an energy dispersive X-ray detector, and signal processing electronic device with a multi-channel analyser. The setup is completed with the vacuum target chamber and/or beam exit; the collected X-ray spectra are processed using suitable software.

For the particulate matter the PIXE technique provides fast, sensitive, non-destructive, multi-element and sensitive analytical tool, however, it strongly depends on the thickness of the filter and its deposits. As emitted X-rays with energies less than approximately 4 keV can be adsorbed in a thick particle deposit of the filter, to provide the best analytical accuracy thin membrane filters should be used with particulate deposits in the range between 10-50 $\mu g\ cm^{-2}$ (Wilson et al., 2002). For this reason, when PIXE is considered for the elemental characterisation of PM, it is important to adjust the sampling interval according to the existing levels of ambient PM in order not to overload the respective filters.

For the purpose of this analysis, filters with particulate samples collected during 12 h were used. Each filter was cut in half. One half was analysed without any further preparation by PIXE, whereas the other part of filter was kept for possible replicates and for analysis of individual particles.

PIXE analysis was carried out at a Van de Graaff accelerator, in vacuum. The PM deposit on filter was bombarded by high-energy protons resulting in characteristics X-rays. For each of the samples two X-ray spectrum were taken; one with a 1.2 MeV proton beam and no absorber in front of the Si(Li) detector for low energy X-ray elements, and another with a 2.25 MeV proton beam and a 250 μm Mylar® filter to detect elements with atomic number higher than 20. The beam area at the target was 20 mm^2. Spectra deconvolution was performed with the AXIL computer code V3.0 and quantitative analysis was carried out with the DATTPIXE package (Alves et al., 1998; Freitas et al., 2003).

3.2.2 Individual particle analysis

Individual particle analysis of PM_{10} and $PM_{2.5}$ was performed by scanning electron microscopy (SEM), using a JEOL JSM-6301F scanning electron microscope equipped with system for X-ray microanalysis by energy dispersive spectrometer NORAN VOYAGER (EDS) analysing elements from carbon to uranium. Elements with atomic numbers lower than 6 were not determined as well as carbon and fluorine due to their presence on the filter substrate.

Two dimensional view of SEM allows measurement of the physical diameter (D_{phys}) of the analysed particles. However, sampling equipment separates PM_{10} and $PM_{2.5}$ according to their aerodynamic diameter (D_{aero}). Therefore, to characterise $PM_{2.5-10}$ and $PM_{2.5}$ particles through SEM, D_{aero} needed to be related with D_{phys} through the following equation (Eq. 3.1) (Conner et. al., 2001):

$$D_{aero} = \chi D_{phys} \sqrt{\rho} \qquad \text{(Eq. 3.1)}$$

where ρ is particle density, and χ is a shape factor specific to SEM that accounts for aerodynamic behaviour and particle orientation on the collected filter substrate. χ was considered equal to 0.81 according to experimental determinations previously published that analysed in detail aerodynamic behaviour of atmospheric particles and their consequent SEM analysis (Willis et al., 2002; Conner et. al., 2001). The minimum D_{phys} for $PM_{2.5-10}$ fraction was set at 3 μm so that particle D_{aero} could be greater than 2.5 μm (Eq. 3.1); the maximum D_{phys} was set at 12 μm, so that particle aerodynamic diameters could be smaller than 10 μm (Eq. 3.1).

For each selected filter 1 cm^2 was cut from the centre of the filter, and mounted with a double-side tape on an aluminium stub. For better conductivity and reduction of electron charge, the sample was coated with carbon layer. The backscattered electron mode was used for particle location and morphological analysis. Microscope magnification of 540 was used to analyse the $PM_{2.5-10}$ particles, allowing detection fields of 70 μm × 160 μm. $PM_{2.5}$ particles were analysed with a magnification of 2000 which allowed the detection field of 50 μm × 40 μm. About 25 fields per each selected filter were observed with 10 randomly selected particles on each field, giving approximately 250 manually characterised particles per filter.

In total 1000 particles were manually analysed to obtain a representative sample, choosing the centre of each particle and using acceleration voltage of 20 kV and X-ray spectrum acquisition time of 60 s.

All images, acquired for each field and particle, were used to manually measure the following morphological parameters: particle area, shape aspect, physical diameter (minimum, maximum and mean), Ferret diameter - distance between two points of the bounding rectangle that would enclose the particle area - (minimum, maximum and mean), and perimeter; for that Image Pro® Plus The Proven Solution ™ software from Media Cybernetics, Inc. was used. Particle roundness was calculated with the parameters (perimeter and area) measured in the images of particles using the following equation (Eq. 3.2).

$$Roudness = \frac{perimeter^2}{4\,\pi\,area} \qquad \text{(Eq. 3.2)}$$

3.2.3 Carbonaceous species

The analysis of elemental and organic carbon was performed using a Shimadzu Total Organic Carbon Analyser TOC-V_{CSH} 5000 (Shimadzu Corporation, Kyoto, Japan) with a solid sampler module (SSM-5000a). The samples were combusted at 900 °C (99.9% O_2, flow of 500 mL min^{-1}) and oxidised using a mixture of cobalt oxide and platinum catalysts in a furnace to produce CO_2, which was then measured by nondispersive infrared spectrophotometer (NDIR).

To analyse different species of carbon in PM_{10} and $PM_{2.5}$, the filters were cut in half and weighted (Mettler Toledo AG245 analytical balance with reading accuracy of 10 μg). One half of the filter was then analysed without any pre-treatment in order to obtain total carbon content.

The other half of filter was used to determine the elemental carbon. For that, each sample was placed in oven at 350 ºC and heated for 15 min to remove the organic carbon (Chen et al., 1997); consequently the filters were analysed by TOC analyser under the same analytical conditions as total carbon.

Organic carbon was then obtained as a difference between total and elemental carbon, assuming that inorganic carbon content is negligible (Sharma et al., 2005).

Glucose (Sigma-Aldrich) was used as the standard for the calibration curve of carbon analysis. Each calibration curve had at least seven points, each point was done in quadruplicate. In all analyses the filter blanks were measured.

Filter handling was cautious using medical forceps; all used materials were regularly cleaned.

3.2.4 Polycyclic aromatic hydrocarbons

PAHs in PM_{10} and $PM_{2.5}$ were determined by microwave assisted extraction (MAE) combined with liquid chromatography (LC). MAE allows selective extraction of compounds in a relatively short time, compared to conventional methods. Another advantage of this technique is usage of less toxic solvents; in comparison with conventional processes, it also requires less solvent and energy, generating fewer wastes.

Dibenzo[a,l]pyrene (estimated to have a carcinogenic potency approximately 100 times higher than benzo[a]pyrene) and 16 PAHs identified as priority pollutants by USEPA (Shibamoto, 1998) were selected for quantification in PM_{10} and $PM_{2.5}$: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene.

The microwave assisted extraction of PAHs was performed by MARS-X 1500 W Microwave Accelerated Reaction System for Extraction and Digestion (CEM, Mathews, NC, USA), configured with a 14 position carousel. The conditions of PM_{10} and $PM_{2.5}$ extraction processes were previously optimised (Castro et al., 2009). Filters with PM were transferred to the glass extraction vessels and 30 mL of acetonitrile (Sigma-Aldrich) was added to each filter. The MAE of both PM_{10} and $PM_{2.5}$ was performed for 20 min at 110 ºC, after that extraction vessels were allowed to cool at room temperature. The extracts were then carefully filtered through a PTFE membrane filter (0.45 µm) and reduced to a small volume using a rotary evaporator (Buchi Rotavapor, R-200) at 20 ºC. A gentle stream of nitrogen was used to dry the extracts under low temperature; the residue was then re-dissolved in 1.0-4.0 mL of acetonitrile, according to the masses of particles the residues were obtained from.

Extracts were analysed using a Shimadzu LC system (Shimadzu Corporation, Kyoto, Japan) equipped with a LC-20AD pump, DGU-20AS degasser and photodiode array SPD-M20A

(PAD) and fluorescence RF-10AXL (FLD) detectors on line. Separation of the compounds was performed in a C18 column (YMC, MP-PAH C18, 50×4.0 mm; 3 µm particle size) maintained at room temperature. The injected volume was 15.0 µL. A mixture of water and acetonitrile was used as the mobile phase. The initial composition of this mobile phase was 45% of acetonitrile and 55% of water (ultra-pure grade, prepared by Milli-Q simplicity 185 Millipore system, Millipore, Molsheim, France) and a linear gradient to 100% was programmed in 15 min, with a final hold of 7 min. Initial conditions were reached in 3 min and maintained for 10 min before next run. The total run time was 35 min with a flow rate of 0.8 mL min^{-1}. Fluorescence wavelength programming was used to perform better sensitivity and minimal interference. Each compound was detected at its optimum excitation/emission wavelength pairs: 315/260 nm (naphthalene, acenaphthene and fluorene), 366/260 nm (phenanthrene), 430/260 nm (anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and dibenzo[a,l]pyrene), and 505/290 nm (indeno[1,2,3-cd]pyrene). Acenaphthylene, which does not show fluorescence, was analysed at 254 nm in PAD. Each analysis was performed at least in triplicate. All materials used for MAE-LC analysis were regularly cleaned in acetone (Fluka, commercial grade), and hexane (supplied by Valente & Ribeiro, commercial grade).

The summary of PM sampled outdoors is presented in Table 3.1.

Table 3.1 Summary of outdoor monitoring campaigns

Campaign	Elemental composition	Carbonaceous species	PAHs
Period	Winter 2004-2005	Summer 2005	Winter 2008
Total duration (days)	82	90	60
Sampling interval (h)	12	24	24
Analytical technique	PIXE, SEM-EDS	Thermal combustion	MAE-LC
Sites	Tr_1, Tr_2, Bc_1, Bc_2	Tr_1, Tr_2, Bc_2	Tr_2, Bc_2
Filter	PTFE (Pall Life Science Teflo™)	Quartz fibre (Schleicher & Schuell)	PTFE (SKC Ltd)

3.3 Indoor air

3.3.1 Characterisation of monitoring sites

For the purposes of this work, the indoor monitoring of PM_{10} and $PM_{2.5}$ was performed at five sites. Three sites were directly influenced by tobacco smoke, one office (Ts_1), one cafeteria (Ts_2), and one home with smokers (Ts_3), whereas other two sites (homes) were used for comparison not being directly influenced by tobacco smoke (reference Rf_1 and Rf_2).

To avoid influence of dissimilar outdoor PM, which commonly penetrate indoors (Ohura et al., 2004; Geller et al., 2002), all monitoring sites were located in the same district (Paranhos); if possible, on the same floor and in the same block of apartments. The number of occupants during sampling as well as other characteristics, such as the presence and use of electronic and cooking devices, cleaning activities and room ventilation, are shown in Table 3.2. Mechanical ventilation did not exist at the monitoring sites; natural ventilation was provided by opening windows as occupants thought necessary. During the monitoring periods detailed diaries of all activities for further observation were kept.

For further descriptions of the monitoring sites, the average CO_2 levels were also measured (Accuro Gas Detector Pump ARNM-F002 supplied by Dräger Sicherheitstechnik GmbH, Germany).

3.3.2 PM sampling

The collection of PM_{10} and $PM_{2.5}$ was performed using procedures described in Sections 3.1.3 and 3.1.4.

3.3.3 Chemical characterisation

Methodologies used to determine elemental bulk composition, carbonaceous species, and PAHs in PM_{10} and $PM_{2.5}$ were identical to those described in Sections 3.2.1, 3.2.3 and 3.2.4.

Table 3.2 Characterisation of indoor monitoring sites

Site	Ts_1	Ts_2	Ts_3	Rf_1	Rf_2
Type	office	cafeteria	home	home	home
Smoking	yes	yes	yes	no	no
No. occupants	1	397[a]	2	1	3
Ventilation	natural	natural	natural	natural	natural
Central heating	yes	-	-	-	yes
Double glazed windows	yes	-	-	-	yes
Cooker	-	electric	electric	electric	electric
Cooking frequency	-	all day	once per day	two-three times per week	once per day
Cleaning frequency	daily	daily	three times per week	daily	three times per week
Floor	2	0	4	4	4
Outdoor traffic	moderate	moderate	moderate	moderate	moderate
Other	uncontrolled ventilation				2 pets, often ventilations, constructions

[a]Mean estimated between 1.00-2.00 p.m.

3.3.4 Individual particle analysis

The analysis of individual particles was performed by an FEI Quanta 400FEG high resolution scanning electron microscope equipped with system for X-ray microanalysis by energy dispersive spectrometry (energy dispersive spectrometer EDAX Genesis X4M analyzing elements from boron to uranium). Elements with atomic number lower than 6 were not determined; carbon and fluorine were determined but mostly not quantified due to their presence on the filter substrate.

To characterise $PM_{2.5}$ and $PM_{2.5-10}$ particles through SEM, D_{aero} needed to be related with D_{phys} using the procedure described in Section 3.2.2.

For each selected filter 1 cm^2 was cut from the centre of the filter, and mounted with a double-side tape on an aluminium stub. For better conductivity and reduction of electron charge, the sample was coated with a carbon layer. The particle location and morphology were automatically detected by an increase in backscattered electron video signal above a present video threshold. Microscope magnification of 5000 was used to analyse the $PM_{2.5-10}$ particles, allowing detection fields of 59 μm × 47 μm. $PM_{2.5}$ particles were analysed with a magnification of 10000 which allowed the detection field of 29 μm × 23 μm. About 280 fields per each selected filter were observed with (at most) 10 randomly selected particles on each field, giving approximately 1000 automatically characterised particles per filter. In total 4000 particles were automatically analysed to obtain a representative sample, choosing the centre of each particle and using acceleration voltage of 20 kV and X-ray spectrum acquisition time of 35 s live time.

All images acquired for each particle were used to manually measure the morphological parameters as described in Section 3.2.2.

Table 3.3 presents the summary of PM indoor monitoring campaigns.

Table 3.3 Summary of indoor monitoring campaigns

Campaign	Elemental composition	Carbonaceous species	PAHs
Period	Winter 2006-spring 2007		Winter 2008
Total duration (days)	112		30
Sampling interval (h)	12	12	12
Analytical technique	PIXE, SEM-EDS	Thermal combustion	MAE-LC
Sites	Ts_1, Ts_2, Rf_1, Rf_2		Ts_3, Rf_1
Filter	PTFE (SKC Ltd)	Quartz fibre (SKC Ltd)	PTFE (SKC Ltd)

3.4 Statistical methods

For the data treatment of PM, the Student's t-test was applied to determine the statistical significance ($P<0.05$, two tailed) of the differences between the means determined for both sites.

Cluster analysis (CA) was used for classification of individual particles. CA is a method that divides the data in classes (clusters) (Manly, 1994), so that objects (particles) in the same cluster (group) would be similar to each other and different from objects in other clusters (Kannel et al., 2007). CA was applied to identify the main groups of particles according to their similarity of elemental composition and morphological parameters. Euclidean distance was used to compute the distance and the clustering procedure was the average linkage method. This procedure is based on the average distance between all pairs of objects belonging to different clusters. Two objects with the lowest average distance are linked to form a new cluster. The complete procedure is presented as the following: (1) determination of the distances between all objects; (2) linkage of two objects that correspond to the lowest distance and recalculation of distances; (3) repetition of step (2) until all objects are in one cluster. The ideal number of clusters to establish may be determined graphically through a dendrogram, - a tree diagram commonly used in cluster analysis (McKenna, 2003).

3.5 References

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4. Results and discussions

4.1 Outdoor air

4.1.1 PM_{10} and $PM_{2.5}$ concentrations

The means and other statistical parameters of PM_{10} and $PM_{2.5}$ measured at two sites influenced by traffic emissions (Tr_1, Tr_2) and at two background sites (Bc_1, Bc_2), as previously described in Sections 3.1.3 and 3.1.4, are shown in Figure 4.1. The statistical analysis of these results indicated that: i) PM_{10} and $PM_{2.5}$ concentrations were significantly lower at the background sites than at the traffic ones; ii) the differences observed between PM_{10} means (as well as between $PM_{2.5}$ means) at site Tr_1 and Tr_2 were not statically significant; iii) PM_{10} and $PM_{2.5}$ means were not significantly different at sites Tr_1, Bc_1 and Bc_2, demonstrating that most of PM_{10} fraction was composed by $PM_{2.5}$; and iv) PM_{10} means at Bc_1 and Bc_2 were significantly different while no difference was observed for $PM_{2.5}$.

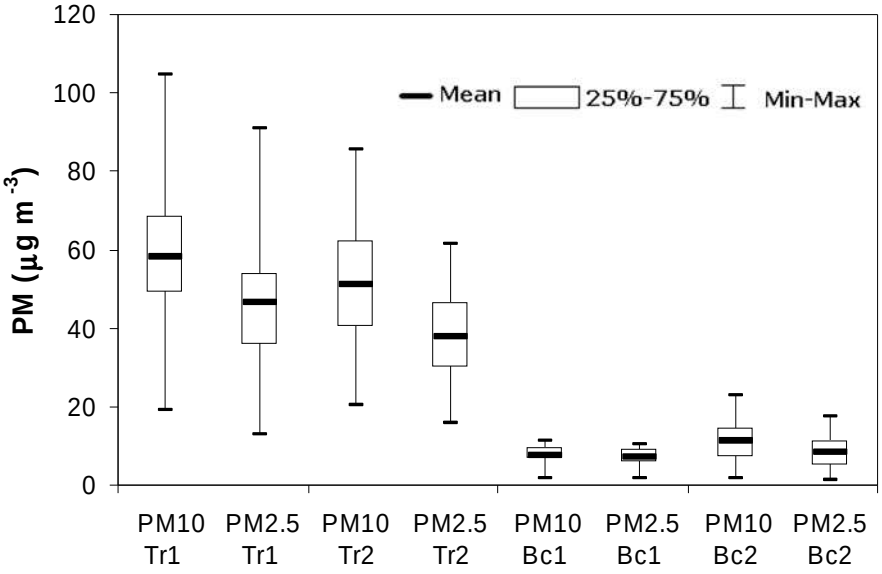


Figure 4.1 Atmospheric concentrations of PM_{10} and $PM_{2.5}$ measured at four sites in Portugal: means, minima and maxima values, 25^{th} and 75^{th} percentiles.

In addition, it was found that at both Tr_1 and Tr_2 PM_{10} concentrations were well correlated with $PM_{2.5}$ as the correlation coefficient square (R^2) is 0.92 (Figure 4.2), indicating that PM_{10} and $PM_{2.5}$ at these sites were influenced by similar sources. In general, the results showed that traffic emissions increased about 370-680% for PM_{10} concentrations and about 360-750% for $PM_{2.5}$ concentrations.

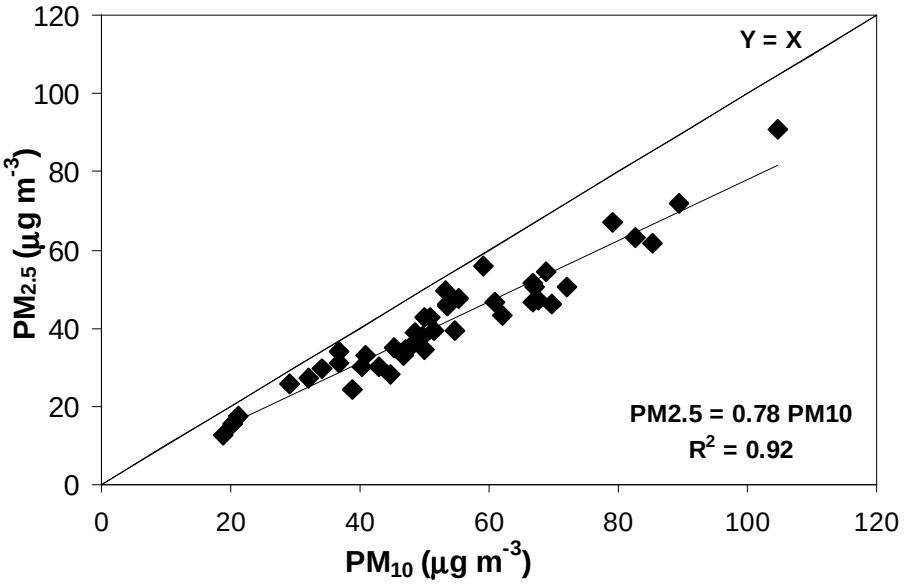


Figure 4.2 $PM_{2.5}$ and PM_{10} correlation for the traffic sites.

PM levels during different periods of week were also compared. It was observed that concentrations of PM_{10} differed significantly for weekends and weekdays at both traffic sites (Table 4.1); the same conclusion was found for $PM_{2.5}$. Corresponding with the traffic patterns, PM_{10} and $PM_{2.5}$ concentrations were lower during the weekends at Tr_1 and Tr_2, whereas no trend was observed for the backgrounds sites, since no direct anthropogenic influence was observed at these sites. The $PM_{2.5}/PM_{10}$ ratios were calculated from each measurement and the means of $PM_{2.5}/PM_{10}$ are also shown in Table 4.1. Weekend $PM_{2.5}/PM_{10}$ ratios were higher than weekday ones at both traffic sites, probably due to different daily routines during the weekends and weekdays.

Table 4.1 Weekend (WE) and weekday (WD) mean values of PM_{10}, $PM_{2.5}$ and $PM_{2.5}/PM_{10}$ at four sites

Site	PM_{10} ($\mu g\ m^{-3}$)		$PM_{2.5}$ ($\mu g\ m^{-3}$)		$\frac{PM_{2.5}}{PM_{10}}$	
	WE	WD	WE	WD	WE	WD
Tr_1	41.1	66.9	34.5	52.2	0.82	0.77
Tr_2	45.9	53.2	36.9	38.8	0.80	0.73
Bc_1	9.5	6.9	8.6	6.6	0.89	0.96
Bc_2	8.9	11.3	5.7	8.5	0.58	0.73

To study the relationship between both PM fractions, the $PM_{2.5}/PM_{10}$ ratios were analysed with more details in Table 4.2.

Table 4.2 Statistics for $PM_{2.5}/PM_{10}$ ratios at four sites

Site	$\frac{PM_{2.5}}{PM_{10}}$ mean	SD	Min	Max	25^{th} percentile	Median	75^{th} percentile
Tr_1	0.79	0.07	0.67	0.92	0.76	0.78	0.83
Tr_2	0.75	0.07	0.62	0.86	0.70	0.74	0.80
Bc_1	0.91	0.05	0.83	0.99	0.88	0.91	0.96
Bc_2	0.72	0.15	0.41	0.94	0.64	0.77	0.81

Table 4.2 shows that during the monitoring campaigns the differences observed between the means of the ratios at both traffic sites and Bc_2 were not statistically significant; however, $PM_{2.5}/PM_{10}$ ratios were slightly higher at site Tr_1 and Tr_2. The mean ratio obtained at site Bc_2 (0.72) was the lowest of all sites. As mentioned previously, site Bc_2 was located close to the seacoast. Sea salt sprays are mainly composed by particles of PM_{10} which justified the lower values there observed for $PM_{2.5}/PM_{10}$. This conclusion was also supported by the comparison

of PM levels (Figure 4.1). The means of PM_{10} were significantly lower at Bc_1 (distant from the seacoast) than at Bc_2 (close to the seacoast); nevertheless, as $PM_{2.5}$ concentrations were not significantly different, the difference in the ratios can be justified by the differences in PM_{10} concentrations. Thus, the obtained result showed that sea salt spray plays an important role as particle source in coastal areas of Portugal and its contribution to PM_{10} particle distributions should be assessed.

The highest mean ratio (0.91) was observed at site Bc_1. This value indicates that this background PM_{10} was mostly composed of $PM_{2.5}$.

It should be enhanced that $PM_{2.5}/PM_{10}$ ratios at the sites not influenced by sea salt spray were relatively high when compared with other sites of similar characteristics in other European countries (Van Dingenen et al., 2004). Once PM_{10} concentrations were not lower, it means that $PM_{2.5}$ concentrations were relatively high in the studied areas even in background environments. As $PM_{2.5}$ have strong influence on lung diseases, this information is relevant for the development of strategies to protect the public health (Maynard and Howard, 1999).

4.1.2 Bulk elemental composition

The emissions of particles related to traffic are consequence of fuel combustion, vehicular component wear, road degradation and roadway maintenance. The traffic-related PM include in their compositions metallic elements with anthropogenic origin such as V, Cr, Fe, Ni, Cu, Zn, Pb (Sansalone and Buchberger, 1997), and also elements resulting from crust and road abrasion such as Mg, Al, Si, K, Ca and Ba (Viana et al., 2006). The following 20 elements were identified by PIXE technique, as described in Section 3.2.1, in PM_{10} and $PM_{2.5}$ sampled at the two traffic and two background sites: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Br, As, and Ba; however, as the number of PM samples with As, Ba and Br was not significant, these elements were not included in further evaluations. The mean concentrations of elements in PM_{10} and $PM_{2.5}$ and the SD at the traffic and the background sites are presented in Table 4.3.

The results demonstrated that: i) at both traffic sites the levels of Mg, Al, Si, P, S, Cl, K and Ca in both fractions were significantly higher than at the background sites; ii) the highest levels of Ti, Cr, Mn, Fe, Ni, Cu and Zn in PM_{10} were recorded at Tr_1 being 15-4600% higher than at the background sites; iii) the highest levels of Cr, Mn, Fe, Ni, Cu and Zn in $PM_{2.5}$ were

Table 4.3 Mean concentrations of elements in PM_{10} and $PM_{2.5}$ at the four sites (ng m^{-3})

	Tr_1				Tr_2				Bc_1				Bc_2			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Mg	111	54.3	45.2	40.7	127	83.6	43.5	29.0	24.3	13.3	22.3	9.59	30.4	21.6	17.3	7.95
Al	1350	941	493	405	1640	808	835	376	401	299	263	230	192	205	105	95.3
Si	2430	1 600	886	657	2360	1 170	1220	637	555	410	395	280	239	294	171	93.1
P	30.2	14.9	19.4	8.70	22.8	11.5	13.2	6.12	9.40	6.49	4.94	4.42	3.67	2.18	0.90	0.24
S	1270	416	1280	434	1010	490	866	357	790	331	847	307	563	566	648	517
Cl	631	405	432	417	957	969	253	230	49.6	19.4	29.1	6.58	567	512	73.4	95.8
K	834	461	632	374	625	246	432	211	166	97.5	147	65.8	70.2	48.3	40.4	36.3
Ca	889	555	275	195	623	336	296	139	89.6	79.7	51.0	41.3	74.9	63.7	28.5	25.4
Ti	50.8	27.4	19.7	12.6	43.5	19.1	25.9	15.1	13.1	9.53	9.88	5.50	8.60	7.41	5.64	5.51
V	14.7	11.0	5.18	3.10	15.5	8.95	9.76	8.42	3.79	3.18	1.27	0.39	1.13	0.46	0.56	0.21
Cr	8.69	3.81	4.55	2.59	6.08	3.41	3.05	2.23	7.64	9.04	1.49	0.39	2.79	0.53	0.72	0.59
Mn	13.4	5.83	11.4	10.2	7.97	3.95	6.63	3.86	3.93	1.92	2.59	2.14	4.38	1.02	1.58	1.34
Fe	1550	671	583	301	810	330	395	194	136	84.7	78.5	62.9	48.7	62.5	31.3	38.4
Ni	8.29	4.46	4.86	4.03	7.41	5.27	5.37	3.90	5.64	5.74	2.19	1.30	-	-	-	-
Cu	87.3	40.2	32.2	17.0	39.0	17.3	18.6	8.60	4.86	3.61	4.26	4.05	1.86	1.52	1.65	1.21
Zn	172	104	134	86.5	104	54.1	83.7	48.7	20.1	15.8	20.2	10.9	7.84	6.42	4.91	3.76
Pb	55.5	27.1	43.4	11.4	33.9	17.0	30.9	17.8	5.83	1.12	10.8	0.88	-	-	-	-

observed at Tr_1 being 110-2600% higher than at the background sites; iv) the highest levels of Pb in PM_{10} were observed at Tr_1, being at the traffic sites 480-850% higher than at Bc_1; v) the highest levels of Pb in $PM_{2.5}$ were recorded at Tr_1, being at the traffic sites 190-300% higher than at Bc_1; vi) the levels of V in PM_{10} at the traffic sites were 290-1300% higher with respect to the background sites; and vii) the levels of V in $PM_{2.5}$ at sites Tr_1 and Tr_2 were 310-1700% higher than at the background sites. As expected, the obtained results showed that at the sites influenced by traffic emissions particle metal contents were significantly higher than at the backgrounds sites. Thus, traffic emissions influenced the compositions of both PM_{10} and $PM_{2.5}$, increasing greatly their metal levels.

The concentrations of all elements in $PM_{2.5}$ versus PM_{10} were also evaluated. For the traffic sites, around 80-90% of S, Mn, Zn and Pb present in PM_{10} were detected in $PM_{2.5}$. This percentage was lower for P, K and Cr (60-80%) and even lower (below 50%) for Mg, Al, Si, Ca, Ti, Fe, and Cu. In general, at both traffic sites the elements originated mostly from anthropogenic activities were predominantly present in $PM_{2.5}$ (S, Mn, Zn, Pb, P, K and Cr) while the elements mostly originated from crust (Mg, Al, Si and Ca) mainly occurred in PM_{10}.

At both background sites, more than 90% of Ti and S present in PM_{10} were found in $PM_{2.5}$; this percentage was lower for Mn (below 63%) and even lower for P (below 50%); however, no further similarities were observed between both background sites. At site Bc_1 more than 90% of Cr, Cu, Zn and Pb present in PM_{10} belonged to $PM_{2.5}$. This percentage decreased for Mg, Al, Si and Ca (60-80%) and dropped below 50% for V. At site Bc_2 more than 90% of Mg, Al, Si and Fe present in PM_{10} belonged to $PM_{2.5}$. This percentage was lower for V, Cu and Zn (60-80%) and even lower (below 50%) for P, K, Ca, Cr and Cl. At site Bc_2, chlorine was mainly present in PM_{10} (42% in $PM_{2.5}$), which was on the contrary to Bc_1, where 70% of Cl present in PM_{10} was detected in $PM_{2.5}$. As it was already referred, Bc_2 was situated close to the seacoast. As sea salt sprays are mostly composed by particles of coarse fraction $PM_{2.5-10}$ the presence of Cl mainly in PM_{10} at Bc_2 can be attributed to marine influence, confirming the previously referred conclusion obtained through the analysis of $PM_{2.5}/PM_{10}$ ratios at two background sites. Concluding, sea salt sprays influence concentrations and compositions of atmospheric background particles as well as the distribution of Cl between PM_{10} and $PM_{2.5}$.

To understand better the distribution of elements between both PM fractions, the elemental concentrations of $PM_{2.5-10}$ were calculated. Figure 4.3 presents the mean ratios of the elemental concentrations (expressed in $\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ for the traffic sites.

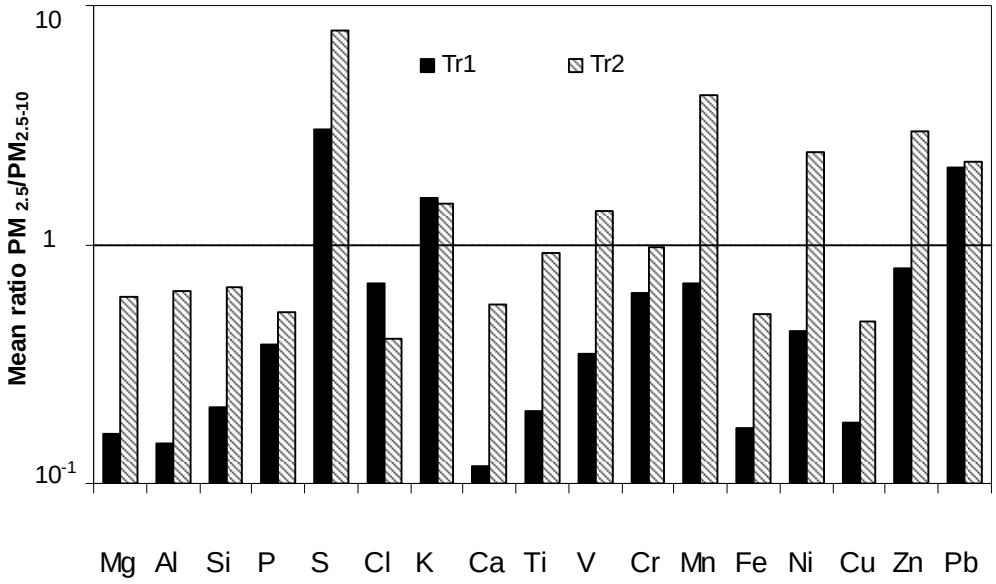


Figure 4.3 Mean ratios of elemental concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ at the traffic sites.

At both Tr_1 and Tr_2, S, K and Pb exhibited ratios higher than 1 being the highest for S; therefore, $PM_{2.5}$ was clearly the more important fraction for those elements. Anthropogenic activities such as traffic, fossil fuel combustions and industrial processes are responsible for emission of those elements mostly in $PM_{2.5}$ (Wei et al., 1999; Querol et al., 2001; Viana et al., 2006) justifying the observed values.

At site Tr_2, V, Mn, Ni and Zn also exhibited ratios higher than 1, showing the importance of $PM_{2.5}$ fraction for these metals. Site Tr_2 was situated near a car park entrance close to the road, where all cars had to slow down and stop to pass the security bars, while the car engines were still running. Therefore, the influence of traffic emissions was probably more direct (Wrobel et al., 2000) at this site than at Tr_1, leading to enrichment of $PM_{2.5}$ in those metals which emissions are usually attributed either to fuel combustion or to the car itself (tyres and breaks abrasions). The presence of V, Mn, Ni and Zn might also be attributed to emissions of other anthropogenic activities such as fossil fuel combustion (V) or industrial processes (Mn,

Ni and Zn). However, if these kind of emissions influenced Tr_2, they should also influence Tr_1 considering the proximity of both sites.

At both Tr_1 and Tr_2, the ratios of elemental composition for Mg, Al, Si, Ca, Ti, Fe and Cu were lower than 1, showing that $PM_{2.5-10}$ was the most important fraction for these elements. The ratios were lower at Tr_1 and the lowest values were observed for Mg, Al, Si and Ca. These are crustal elements usually present in resuspended dust. Tr_1 was situated next to one of the busiest highway where a high number of cars were passing per day, suggesting that the contribution of resuspended dust was stronger than at Tr_2. These results confirmed that the elements related to crust (Mg, Al, Si and Ca) were predominately present in $PM_{2.5-10}$ fraction. The different behaviour of Tr_1 and Tr_2 showed the clear influence of distance between the sampling point and the roads, which is mainly justified by longer atmospheric lifetime of $PM_{2.5}$ and their complicated transport (Hitchins et al., 2000).

The mean ratios of the elemental composition in $PM_{2.5}$ versus $PM_{2.5-10}$ at the background sites were also evaluated (Figure 4.4).

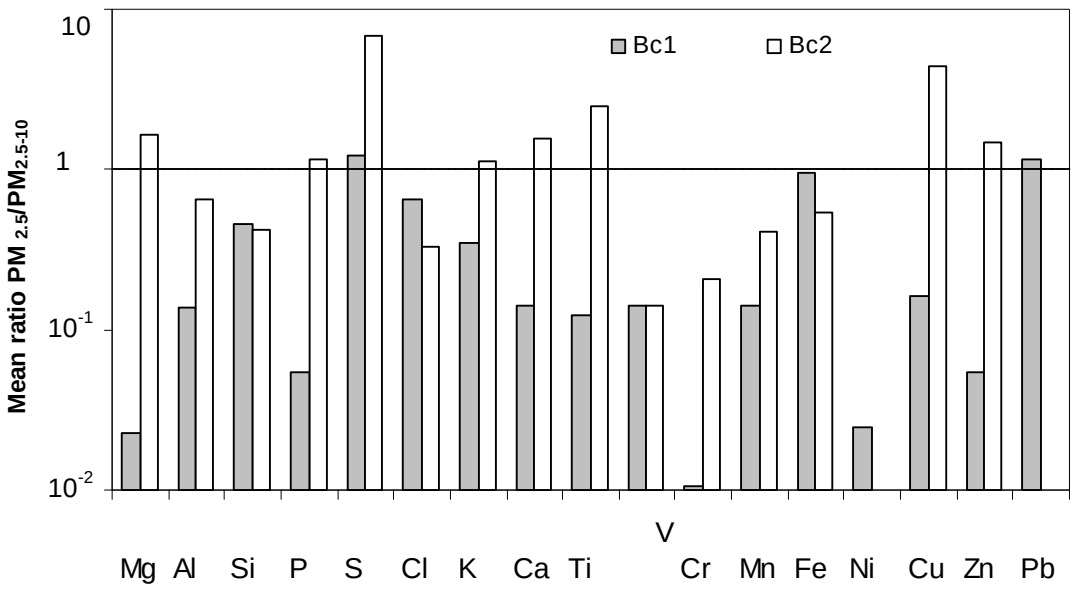


Figure 4.4 Mean ratios of elemental concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ at the background sites.

The behaviours of the background sites were considerably different. At Bc_1, $PM_{2.5}$ was the most important fraction for S and Pb, while at Bc_2, Mg, P, S, K and Ca as well as Ti, Cu and

Zn were predominantly in $PM_{2.5}$ fraction. The main differences observed between the background sites were for Pb and Ni that were present in both PM fractions at Bc_1 but not present at Bc_2. Both background sites were not directly influenced by anthropogenic emissions. Nevertheless, some regional transport of airborne particles can justify the differences observed between Bc_1 and Bc_2.

The previous analyses suggested that some metallic elements may be more gathered in $PM_{2.5}$ than in PM_{10}. To further evaluate this observation and to analyse if crustal source significantly enhanced particle composition, the method of enrichment factor (EFs) was applied (Wei et al., 1999). The calculations were based on the average chemical composition of crust given by Mason (Mason, 1958); aluminium was used as reference element in calculations using the following equation (Eq. 4.1):

$$\mathrm{EF}i = \frac{\left(c_i / c_{Al}\right)_{PM}}{\left(c_i / c_{Al}\right)_{soil}} \qquad \text{(Eq. 4.1)}$$

where c_i is the concentration of element i and c_{Al} represents the concentration of aluminium, in particles (PM) or in soil, as indicated in the subscript. If EF_i>10, element i is considered to come mainly from a non-mineral dust source (non-crustal); if EF_i<10 element i is considered to come mainly from dust and/or soil source (crustal) (Torfs and Van Grieken, 1997). Figure 4.5 shows EFs for PM_{10} and $PM_{2.5}$ at the traffic sites.

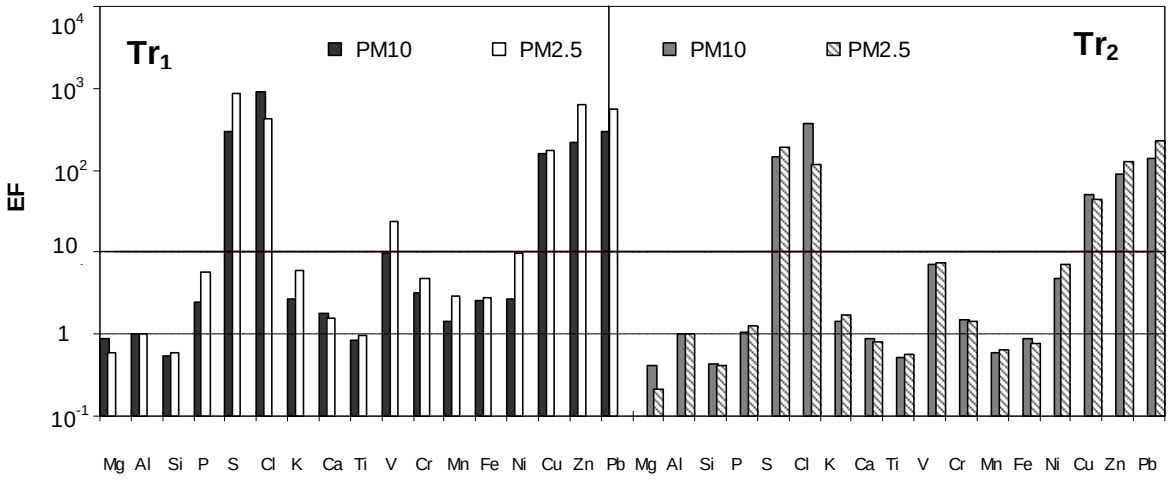


Figure 4.5 Enrichment factors for PM_{10} and $PM_{2.5}$ at two traffic sites.

At Tr_1 and Tr_2 S, Cl, Cu, Zn and Pb exhibited EFs greater than 10 for both PM fractions, being the highest for S and Cl; meanwhile for V, EF was greater than 10 just at Tr_1 for $PM_{2.5}$.

Cl was associated with sea salt spray and the other elements were not of crustal origin. EFs of these elements (S, Cu, Zn and Pb) were higher for $PM_{2.5}$ than for PM_{10}, confirming that anthropogenic activities influenced mainly the particles in $PM_{2.5}$. The higher values of EFs at Tr_1 can be justified by a stronger influence of traffic emissions, because traffic density was considerably higher at this site.

At both background sites (Figure 4.6) EFs greater than 10 were observed for S, Cl, Cu and Zn. At Bc_1 Ni and Pb also exhibited EF greater than 10. At the both background sites Cl exhibited EFs greater than 10 in both PM being significantly higher at Bc_2. These findings confirm the results previously obtained through the analysis of $PM_{2.5}/PM_{10}$ ratios and through the analysis of elemental concentrations in both PM fractions, which showed the strong influence of sea salt spray at Bc_2. It should also be referred that the calculated EFs were significantly higher than those at Lisbon area (Alves et al., 1998), showing that influence of sea salt sprays depends on the region. The EFs for S, Cu, Zn, and Pb showed that the regional transport of anthropogenic emissions also influenced particles at the background sites. Nevertheless, as the observed concentrations were very small it could be concluded that the influence of anthropogenic emissions was not significant. EFs also demonstrated that, at the background sites most elements in the particles were from crustal origin. According to these results both background sites Bc_1 and Bc_2 can be used as reference sites for comparison of results at polluted places.

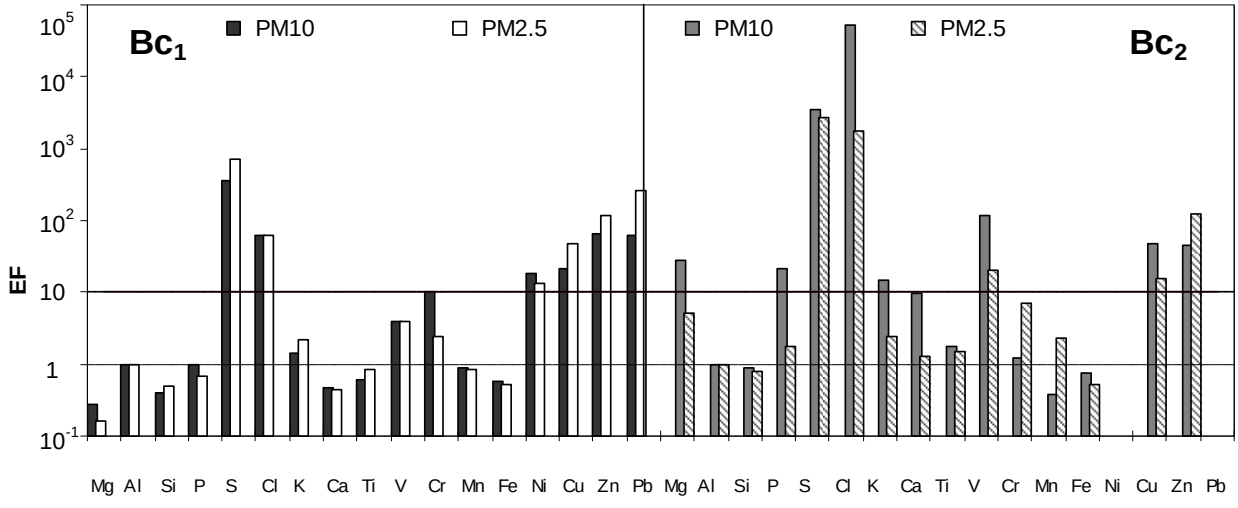


Figure 4.6 Enrichment factors for PM_{10} and $PM_{2.5}$ at two background sites.

4.1.3 Analysis of individual particles

The individual particles were analysed for one site influenced by traffic emissions (Tr_2) and at one background site (Bc_2); Table 4.4 shows the daily statistics for PM masses at these sites.

Table 4.4 Daily statistics for $PM_{2.5}$ and $PM_{2.5-10}$ masses at the traffic and background sites

Site	Traffic		Background	
	$PM_{2.5}$ μg/day	$PM_{2.5-10}$ μg/day	$PM_{2.5}$ μg/day	$PM_{2.5-10}$ μg/day
Mean	1050	360	219	75
SD	313	179	122	44
Min	430	120	35	10
Max	1690	650	470	195
25^{th} percentile	817	203	133	46
Median	995	370	223	68
75^{th} percentile	1290	468	306	100

A mean of 1410 μg of PM_{10} was collected per day at site Tr_2 being fractioned into $PM_{2.5}$ (daily mean: 1050 μg) and into $PM_{2.5-10}$ (daily mean: 360 μg). At the background site a mean of 294 μg of PM_{10} was collected per day, being fractioned into $PM_{2.5}$ (daily mean: 219 μg) and into $PM_{2.5-10}$ (daily mean: 75 μg). From these results it is obvious that at both sites $PM_{2.5}$ accounted for most of PM_{10}.

In all analysed $PM_{2.5}$ and $PM_{2.5-10}$ samples collected at sites Tr_2 and Bc_2 the presence of the following 25 elements was determined by SEM-EDS analysis, as described in Section 3.2.2: Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Pb, La, Ce, Ti, Ba, Mo, Cr, Co, V, Ni, Sn and Sb. Figure 4.7 presents the mean weight percentages of all identified elements in 1000 particles at the traffic and background sites for $PM_{2.5}$ and $PM_{2.5-10}$.

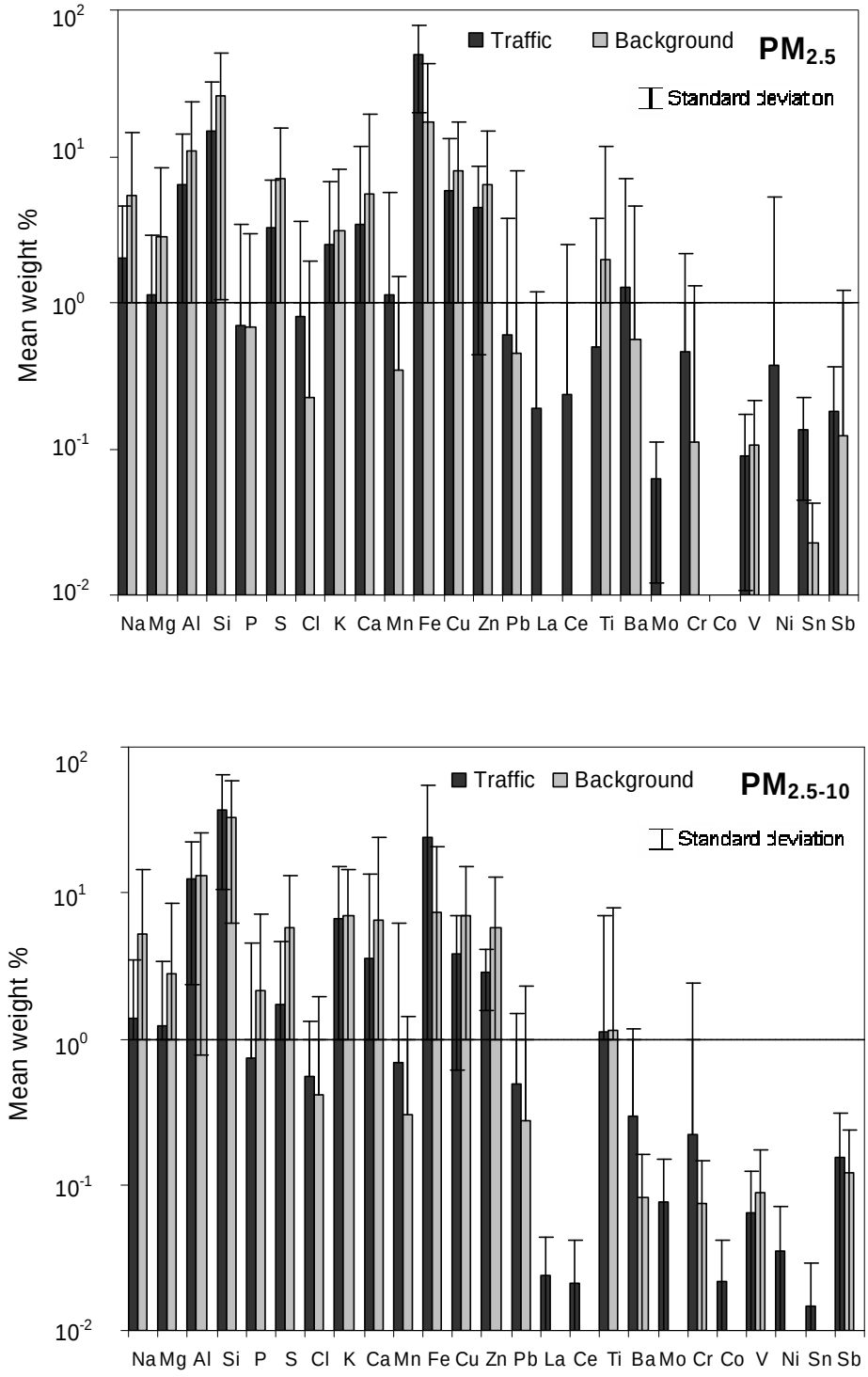


Figure 4.7 Mean weight percentages of all elements determined by SEM-EDS in $PM_{2.5}$ and $PM_{2.5-10}$.

In order to study the influence of traffic emissions on PM, the SEM-EDS analysis of individual particles in $PM_{2.5}$ and $PM_{2.5-10}$ was performed to evaluate their chemical compositions and morphological parameters. CA method was applied to 1000 particles allowing the identification of the main groups of particles according to their similar chemical

compositions and morphological characteristics, aiming the identification of the respective emission sources.

Figure 4.8 shows the main identified groups of particles in $PM_{2.5}$ at the traffic site; the means of morphological parameters of these groups are presented in Table 4.5.

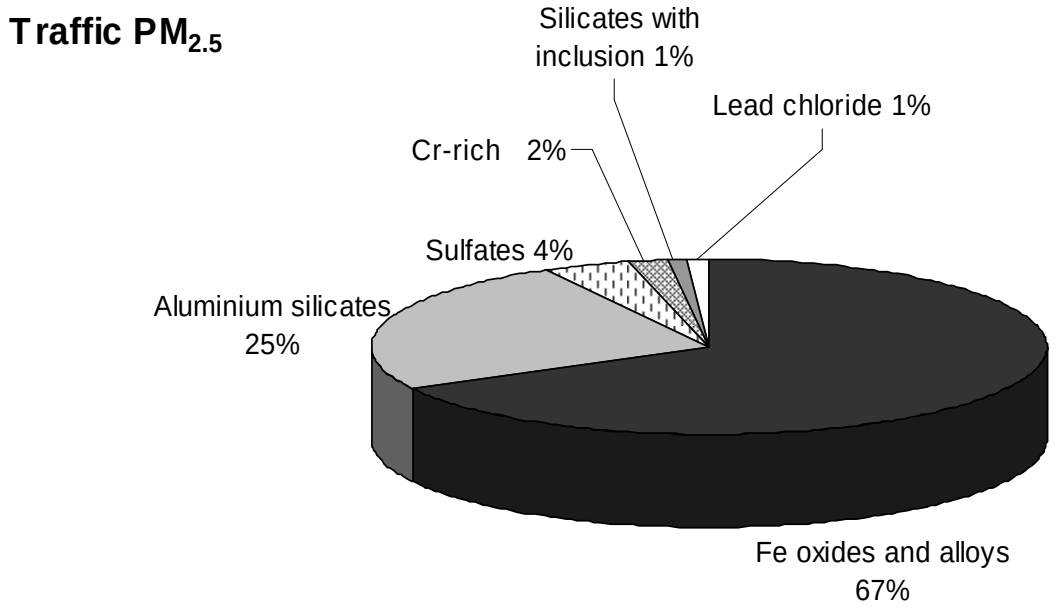


Figure 4.8 Main groups of particles in $PM_{2.5}$ identified by CA method at the traffic site.

It is clear that the dominating group of this fraction was Fe oxides and alloys (67%). These particles contained high amount of Fe in the form of oxides and alloys, accompanied by other metals such as Cu, Zn, Pb, Ni, and Cr, which allowed concluding that they could be originated from traffic and industrial sources (Moreno et al., 2003). As no significant industrial source was identified within the direct proximity of this site, traffic emissions were considered as the main source of these particles. The second most abundant group of $PM_{2.5}$ particles was constituted by aluminium silicates (25%) having high content of Al, Si, and K; these particles were originated most likely from crustal sources. The third most abundant group of particles in traffic $PM_{2.5}$ was constituted by sulfates (4%) that can be also formed as secondary particles. This group was especially rich in gypsum ($CaSO_4.2H_2O$) that can be traced to both natural and anthropogenic sources through weathering of natural minerals

Table 4.5 Means of abundances and morphological parameters of particles identified in $PM_{2.5}$ at the traffic site

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Fe oxides and alloys	67	1.22	1.49	0.88	1.40	1.13	0.96	1.45	1.23	3.83	1.19
Aluminium silicates	25	4.92	1.53	1.75	3.03	2.35	2.05	3.11	2.63	8.50	1.25
Sulfates	4	4.63	1.37	1.76	2.97	2.29	2.08	3.01	2.60	8.76	1.36
Cr-rich	2	1.79	1.52	0.97	1.70	1.34	1.12	1.74	1.47	4.53	1.05
Lead chloride	1	3.84	1.26	1.56	2.08	1.83	1.68	2.13	1.93	5.99	1.04
Silicates with inclusion	1	0.27	1.78	0.45	0.80	0.63	0.42	0.78	0.61	1.80	1.01

or buildings made from such material, the latter being very common in Oporto (Begonha, 1997). The remaining groups of particles in traffic $PM_{2.5}$ showed considerably lower abundance: Cr-rich particles (2%) originated most likely from other anthropogenic sources, and silicates with mineral inclusion (1%). These particles with high proportions of Si, La, and Ce were probably silicates with inclusions of La and Ce, rare elements not common in atmospheric particles. As no source of particles with those elements was observed at this site or within its proximity, this group of particles probably resulted from long-distance transport of atmospheric particles. The least abundant group was identified as lead chloride. In the past, tetraethyl lead was added to petrol to increase the octane number, and 1, 2 dibromethane was also added to remove the lead from the cylinder as $PbBr_2$ (vapour at the heated cylinder) (Xie et al., 2004); consequently, the combustion of leaded fuels in motor vehicles led to $PbBr_2$ emissions, further transformed by atmospheric processes. However, as the use of leaded petrol was stopped in Portugal several years ago and taking into the consideration the very low abundance of this group, it is probable that these particles also resulted from long-distance transport of atmospheric particles, namely from north-Africa (Reis et al., 2002; Querol et al., 2001).

Up to this date, some other studies analysed the origin of atmospheric particles in $PM_{2.5}$ using organic components as tracers (Schauer et al., 1996). The conclusions of those works were consistent with the results of this study, showing that traffic emissions (mainly) and road dust were the major contributors to particles of $PM_{2.5}$ fraction.

Five groups of particles were identified in $PM_{2.5-10}$ fraction at traffic site (Figure 4.9); the means of morphological parameters of these groups are shown in Table 4.6. The dominating group of particles in this fraction was constituted by aluminium silicates (74%) resulting from natural sources, mainly from erosion of local geological formations. The group of silicates is very broad geochemical subdivision including various rocks; it can be further subdivided into mafic (Mg and Fe-rich) and felsic (Si and Al-rich) types (Moreno et al., 2003). The subsoil of Oporto region consists of granite rich in Al and Si. In agreement with that, silicates within $PM_{2.5-10}$ fraction were rich especially in Al, Si and K belonging to the felsic type. Other groups of particles in traffic $PM_{2.5-10}$ included traffic-related Fe oxides and alloys (20%), sulfates (3%, gypsum); Cu-Fe-rich particles (2%) and Mn-rich particles (1%). Copper and its compounds are naturally present in the earth crust; however, it is not the case in Oporto.

Table 4.6 Means of abundances and morphological parameters of particles identified in $PM_{2.5-10}$ at the traffic site

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Aluminium silicates	74	45.36	1.72	4.92	9.68	7.15	6.26	10.09	8.37	28.62	1.67
Fe oxides and alloys	20	16.94	1.62	3.09	5.76	4.4	3.79	5.92	4.98	16.63	1.39
Sulfates	3	35.37	2.00	4.11	9.13	6.65	5.02	9.38	7.44	24.35	1.36
Cu-Fe-rich	2	11.97	1.46	2.73	4.45	3.62	3.22	4.57	3.99	12.40	1.07
Mn-rich	1	10.34	1.32	2.74	3.80	3.33	2.92	4.01	3.56	10.82	1.04

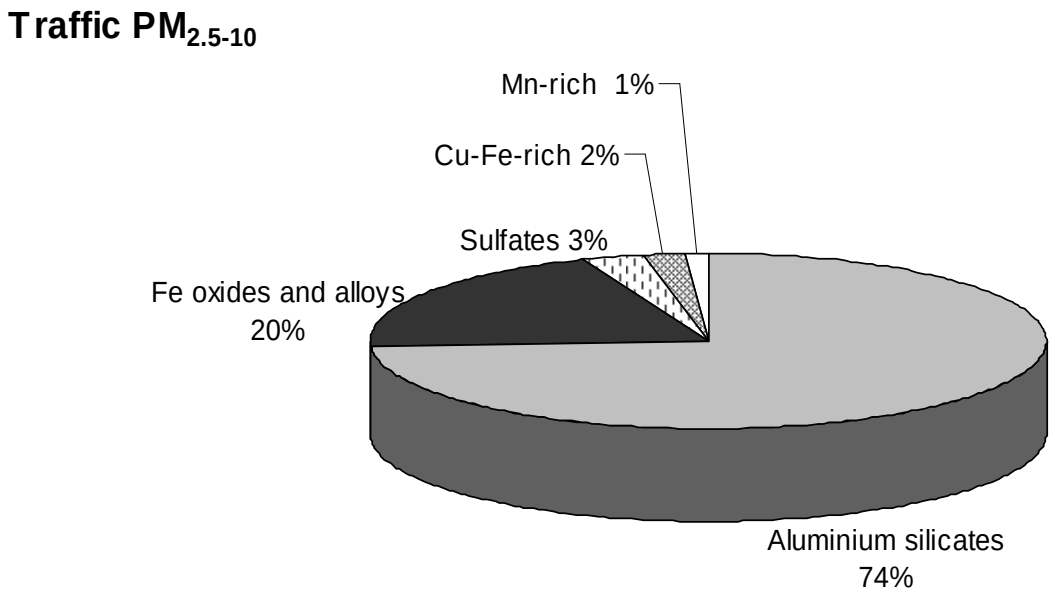


Figure 4.9 Main groups of particles in $PM_{2.5-10}$ identified by CA method at the traffic site.

It was assumed that Cu-Fe rich particles resulted from some anthropogenic sources such as iron and steel production, waste incineration, and from oil and gasoline combustions. The presence of Mn-rich particles, commonly released to air from combustion of fossil fuels, suggested that both Cu-Fe and Mn-rich particles probably resulted from power plant emissions situated about 30 km east of Oporto.

The main groups of particles identified in $PM_{2.5}$ collected at the background site are shown in Figure 4.10; the morphological parameters of these groups are presented in Table 4.7. It is obvious that $PM_{2.5}$ were dominated by aluminium silicates (63%), rich in Al, Si and K, originated from natural sources such as soil. The group of sulfates (15%) was also of a natural origin; as they contained high amount of Na and K, they were sea-related sodium and potassium sulfates. Ti-rich (3%) and Al-rich (0.5%) particles contained, respectively, high percentage of Ti and Al as oxides; these particles could be also attributed to natural origin (soil). Figure 4.11 shows as an example the SEM secondary images of Ti-rich particles. Other two groups identified in background $PM_{2.5}$ probably resulted from anthropogenic sources: Fe oxides and alloys (18%) that could be related to traffic emissions, and lead sulphate (0.5%).

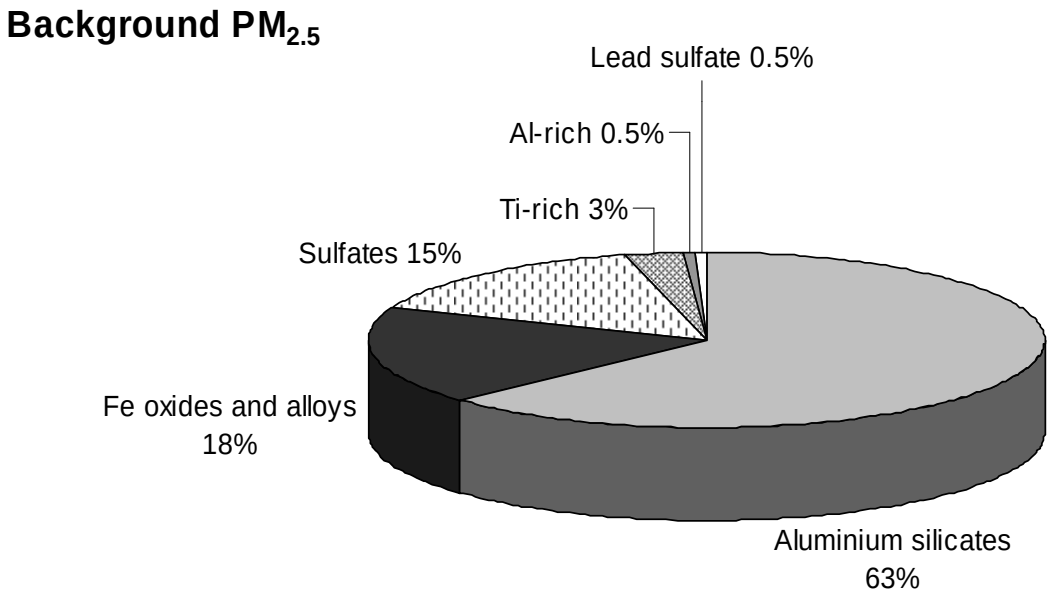
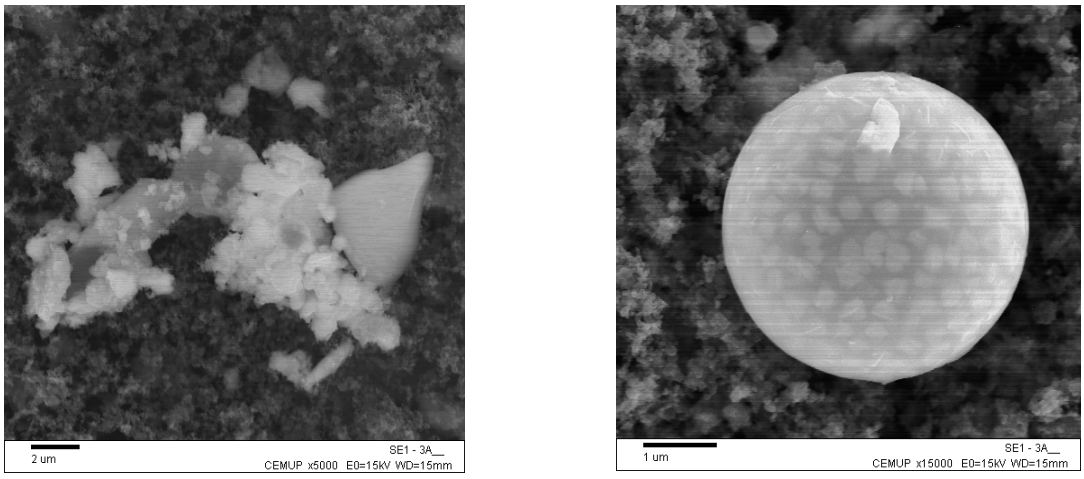


Figure 4.10 Main groups of particles in $PM_{2.5}$ identified by CA method at the background site.



(A) *(B)*

Figure 4.11 Examples of SEM secondary electron images: (A) agglomeration of minerals, (B) Ti-rich particle.

As the background site was situated in a mountain area without direct influences of emission sources, it was concluded that these particles of anthropogenic origin were related to regional transport of atmospheric pollutants; in agreement with previous studies (Wrobel et al., 2000) urban-related (especially traffic-related) particles of $PM_{2.5}$ fraction travel considerably farther from their sources than $PM_{2.5-10}$, probably due to their smaller sizes (Wrobel et al., 2000).

Table 4.7 Means of abundances and morphological parameters of particles identified in $PM_{2.5}$ at the background site

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Aluminium silicates	63	3.93	1.48	1.63	2.54	2.04	1.75	2.59	2.21	6.94	1.18
Fe oxides and alloys	18	0.96	1.48	0.81	1.19	1.00	0.84	1.20	1.04	3.21	1.05
Sulfates	15	3.65	1.79	1.42	2.82	2.06	1.73	2.96	2.41	7.83	1.48
Ti-rich	3	2.54	1.45	1.33	2.09	1.72	1.27	2.12	1.75	5.45	1.08
Al-rich	0.5	2.67	1.15	1.56	2.01	1.79	1.63	2.01	1.87	5.77	1.00
Lead sulfate	0.5	372	0.04	0.21	1.00	0.41	0.67	0.10	0.14	0.21	0.20

The main groups of particles identified in $PM_{2.5-10}$ collected at the background site are shown in Figure 4.12; the morphological parameters of these groups are shown in Table 4.8. Aluminium silicates, rich in Al, Si and K, clearly dominated $PM_{2.5-10}$ fraction with abundance of 73%, being originated from natural sources such as crust and soil; sea-related sulfates with Na and K formed the second most abundant group (19%). Ca-rich particles (6%) were of natural origin present as $CaCO_3$ (limestone) with some impurities, such as Zn, Cu and Si. Limestone is a mineral distributed in crust, found in soils and in road dust, being widely used through its application as building material and cement manufacturing. The least abundant group of particles in background $PM_{2.5-10}$ were Ti-rich particles (2%) probably in the forms of oxide with high impurities of Cu; the specific origin of these particles was not identified.

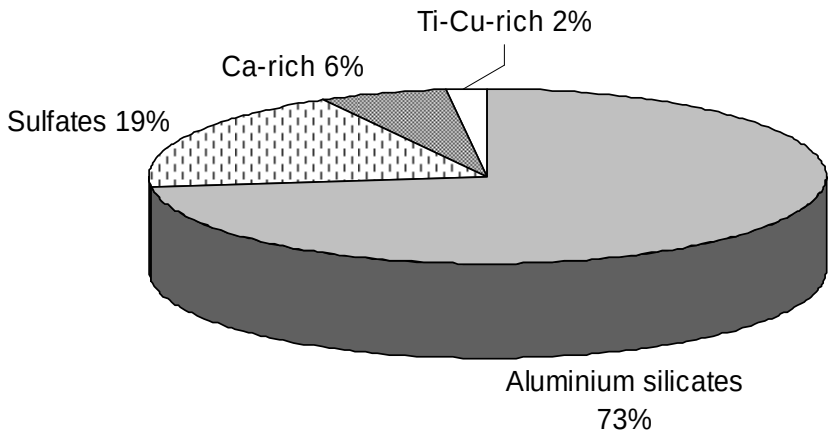


Figure 4.12 Main groups of particles in $PM_{2.5-10}$ identified by CA method at the background site.

Table 4.8 Means of abundances and morphological parameters of particles identified in $PM_{2.5-10}$ at the background site

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Aluminium silicates	73	31.82	1.83	4.03	8.20	5.99	4.97	8.51	6.96	23.52	1.56
Sulfates	19	21.17	1.80	3.27	6.76	4.96	4.15	6.97	5.72	19.45	1.58
Ca-rich	6	21.79	1.67	3.49	6.71	5.05	4.30	7.01	5.79	19.29	1.45
Ti-Cu rich	2	19.05	1.52	3.57	5.88	4.66	4.01	6.09	5.13	16.26	1.19

The analysis of 1000 particles in $PM_{2.5}$ and $PM_{2.5-10}$ collected at the site influenced by traffic emissions and at the background site (Figures 4.8 - 4.12) allowed the following comparison: $PM_{2.5}$ versus $PM_{2.5-10}$ at each site and between sites. Table 4.9 summarises all the groups of particles in $PM_{2.5}$ and $PM_{2.5-10}$ and their origin for traffic and background sites. In general, traffic emissions influenced the compositions of both $PM_{2.5}$ and $PM_{2.5-10}$ at site Tr_2. The particles originated from traffic were predominantly present in $PM_{2.5}$ fraction (3.4 times higher in $PM_{2.5}$ than in $PM_{2.5-10}$). On the contrary, the particles from natural sources, mainly from soils, were predominantly present in $PM_{2.5-10}$ being 3.0 times higher than in $PM_{2.5}$; therefore it could be concluded that particulate emissions originated from natural sources were predominantly present in $PM_{2.5-10}$ fraction.

The comparison of $PM_{2.5}$ between site Tr_2 and Bc_2 also showed significant differences. As expected, the contribution of traffic emissions in $PM_{2.5}$ was 3.7 times higher at the traffic site than at the background one. On the contrary, the contribution of particles from natural sources was significantly higher at the background site being 3.3 times higher. It is also important to emphasise that at the background site the amount of sulfates was 3.8 times higher being of natural origin (sea-related), whereas sulfates at the traffic site resulted mostly from weathering of natural minerals (gypsum) and buildings made from such material. Based on these results, it was confirmed that Bc_2 can be safely used as reference site for comparison of $PM_{2.5}$ at polluted places.

Both $PM_{2.5-10}$ at the background and traffic sites were dominated by aluminium silicate particles from natural sources with almost identical abundances (74% and 73% at Tr_2 and Bc_2, respectively). However, the total contribution of natural sources in $PM_{2.5-10}$ was higher at the background site (98%) due to the contribution of sea-related sulfates; at the traffic site sulfates in $PM_{2.5-10}$ resulted from anthropogenic activities. The most significant difference between $PM_{2.5-10}$ at both sites was the absence of particles of traffic and anthropogenic origin, confirming that the background site can be safely used as reference site.

The results of $PM_{2.5}$ and $PM_{2.5-10}$ at traffic and background sites, previously analysed by PIXE in Section 4.1.2, were consistent with the SEM-EDS ones here analysed. Both PIXE and SEM indicated that $PM_{2.5}$ fraction was dominated by traffic particles whereas $PM_{2.5-10}$ fraction was dominated by natural particles (geological); particles of $PM_{2.5}$ at the background site were influenced by regional transport of atmospheric particles.

Table 4.9 $PM_{2.5}$ and $PM_{2.5-10}$ at the traffic and background sites: abundance of particle main groups (%) and their respective origin

Site	PM fraction	Particle groups	Abundances (%)	Origin	Σ Origin (%)	
Traffic	$PM_{2.5}$	Fe oxides and alloys	67	traffic		
		Aluminium silicates	25	natural	natural:	25
		Sulfates	4	anthropogenic	traffic:	67
		Cr-rich	2	anthropogenic	anthropogenic:	8
		Silicates with inclusion	1	anthropogenic		
		Lead chloride	1	anthropogenic		
	$PM_{2.5-10}$	Aluminium silicates	74	natural		
		Fe oxides and alloys	20	traffic	natural:	74
		Sulfates	3	anthropogenic	traffic:	20
		Cu-Fe-rich	2	anthropogenic	anthropogenic:	6
		Mn-rich	1	anthropogenic		
Background	$PM_{2.5}$	Aluminium silicates	63	natural		
		Fe oxides and alloys	18	traffic	natural:	82
		Sulfates	15	natural	traffic:	18
		Ti-rich	3	natural	anthropogenic:	<1
		Al-rich	0.5	natural		
		Lead sulfate	0.5	anthropogenic		
	$PM_{2.5-10}$	Aluminium silicates	73	natural		
		Sulfates	19	natural	natural:	98
		Ca-rich	6	natural	other:	2
		Ti-Cu-rich	2	other		

To further understand the influence of traffic emissions on public health, the elements with adverse health effects were analysed with more detail. The elements listed as human or animal carcinogens are Cr, Ni, As, Cd, Pb, and Co (ATSDR, 2006). Out of these, the concentrations of Cr, Ni, and Pb were previously determined in both $PM_{2.5}$ and $PM_{2.5-10}$ by PIXE (Section 4.1.2). SEM-EDS analysis determined the presence of Cr, Ni, Pb and Co in $PM_{2.5}$ and $PM_{2.5-10}$ particles (Figure 4.7), allowing further complementarities of previous results. Those analyses showed that Pb and Cr were present in particles of both fractions at both sites (Figure 4.7) while Ni was present in particles of both fractions only at traffic site. Analysing Figures 4.7 - 4.12 together, it was found that Ni was present as a minor element (low concentrations in each analysed individual particle) mainly in Fe oxides and alloys, very abundant especially in $PM_{2.5}$ of the traffic site. Cr and Pb were also mainly present as minor elements enriching Fe oxides and alloys, but both elements appeared as dominant in $PM_{2.5}$ of the traffic site; however, the abundances of those particles were very low (2 and 1%, respectively, for Cr and Pb). Co was not previously determined by PIXE which suggested very low content. However, by SEM-EDS the presence of Co in individual particles was identified. Co was present only in traffic $PM_{2.5-10}$ but in very low concentrations (Figure 4.7), confirming that it was present as a trace element in few particles, the amount not being sufficient to be detected by PIXE (Co was mainly present in 2% of Cu-Fe-rich particles-Figure 4.9). In general it was concluded that Cr, Ni and Pb concentrations determined by PIXE were mainly due to the presence of these elements in trace concentrations in many particles. As these elements cause serious health effects, this information is fundamental for the development of strategies to protect public health. In addition it was found that mean contents of Cr, Ni and Pb (Figure 4.7) were higher in $PM_{2.5}$ than in $PM_{2.5-10}$. Taking into consideration that high ratios of $PM_{2.5}/PM_{2.5-10}$ masses were previously determined (Table 4.4), this information is also important for establishment of new limits for $PM_{2.5}$ concentrations in outdoor air. Concluding, SEM-EDS showed to be a very useful technique to complement elemental analysis of PM fractions.

4.1.4 Carbonaceous species

The concentrations of total carbon, organic carbon and elemental carbon in PM_{10} and $PM_{2.5}$ at two sites influenced by traffic emissions (Tr_1, Tr_2) and at one background site (Bc_2) were determined using the procedure described in Section 3.2.3; Table 4.10 shows the means of all

Table 4.10 Mean concentrations of carbonaceous species in PM_{10} and $PM_{2.5}$ at three sites ($\mu g\ m^{-3}$)

	Tr_1				Tr_2				Bc_2			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
Total carbon	27.1	8.6-66.7	21.2	3.3-59.4	47.7	13.6-102	28.2	9.5-74.8	6.6	3.2-11.6	4.8	2.1-8.2
Organic carbon	15.8	4.66-35.9	13.7	2.6-36.0	27.2	4.2-59.3	17.4	2.7-44.9	4.7	1.6-6.41	3.5	0.58-4.7
Elemental carbon	11.3	1.5-30.8	7.5	1.1-22.4	20.5	5.0-42.4	10.8	3.6-33.6	1.9	0.92-5.5	1.3	0.45-4.5

carbonaceous species in PM_{10} and $PM_{2.5}$ at the respective sites. The results demonstrated that: i) as expected for both PM fractions the concentrations of all carbonaceous species were significantly higher at the traffic sites than at the background one; ii) the highest levels for all carbonaceous species were observed at the site Tr_2; iii) the levels of total carbon at the traffic sites were 310-630% and 340-490% higher for PM_{10} and $PM_{2.5}$, respectively; iv) the levels of organic carbon at the traffic sites were, respectively, 240-480% and 290-390% higher for PM_{10} and $PM_{2.5}$; v) the highest difference were observed for concentrations of elemental carbon, being at the traffic sites 500-900% and 490-740% higher for PM_{10} and $PM_{2.5}$, respectively. Thus, these results clearly showed that traffic emissions strongly increased the levels of all carbonaceous species in both PM_{10} and $PM_{2.5}$.

The weekday and weekend mean concentrations of carbonaceous species in PM_{10} and $PM_{2.5}$ at the traffic (Tr_1, Tr_2) and at the background site (Bc_2) are shown in Figure 4.13. It can be clearly observed that at both traffic sites concentrations of all carbonaceous species in both PM differed significantly between the weekdays and weekends; corresponding with the traffic patterns the concentrations were much higher during weekdays. Being in agreement with previous results, no significant differences were observed between weekday and weekend concentrations of all carbonaceous species at the background site.

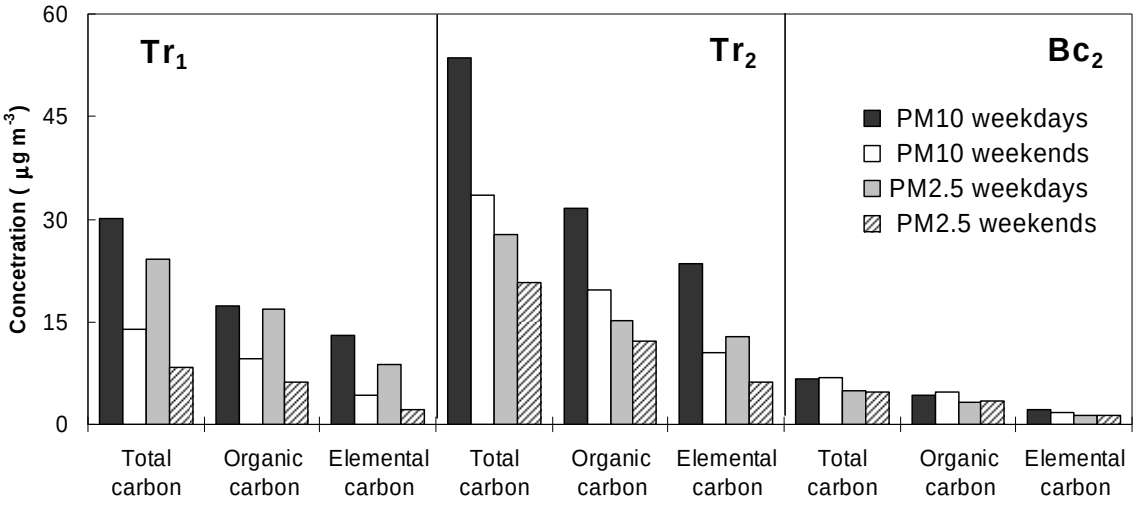


Figure 4.13 Weekday and weekend mean concentrations of carbonaceous species in PM_{10} and $PM_{2.5}$ at three sites.

The contributions of total, organic and elemental carbon to PM_{10} and $PM_{2.5}$ masses at two traffic and one background site were also analysed (Table 4.11).

Table 4.11 Carbonaceous species in PM_{10} and $PM_{2.5}$ masses (%) at three sites

	Tr_1		Tr_2		Bc_2	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
Total carbon	42	53	41	53	27	36
Organic carbon	25	30	25	32	18	23
Elemental carbon	17	23	16	21	9.0	13

At both Tr_1 and Tr_2, PM_{10} showed to have similar percentages of total carbon, (42-41%), whereas organic and elemental carbons contributed, respectively, 25% and approximately 17%. The percentages observed for carbonaceous species in $PM_{2.5}$ mass were also similar at both traffic sites; however, the obtained values were higher, ranging from 21% to 53% for elemental and total carbon, respectively, being similar to other studies (Harrison et al., 2004). In general, these results showed that concentrations of all carbonaceous species differed significantly between both traffic sites (Table 4.10), but their percentages in PM_{10} and also in $PM_{2.5}$ masses were almost identical at both sites influenced by traffic emissions, confirming that these places were mainly influenced by the same sources.

At the background site the percentages of carbonaceous species in PM_{10} and $PM_{2.5}$ masses were considerably different from the traffic ones, with lower percentages observed. At this site 27% of PM_{10} mass was composed by total carbon, whereas organic and elemental carbons contributed, respectively, 18% and 9%; the percentages observed for carbonaceous species in $PM_{2.5}$ mass were higher, ranging from 13% to 36% for elemental and total carbon, respectively. Thus these results indicate that traffic emissions not only increased the concentrations of carbon species in PM_{10} and $PM_{2.5}$ (Table 4.10), but also their percentages in both PM masses.

To study the concentrations of carbonaceous species associated with different sizes of PM, the concentrations of total, organic and elemental carbons in particles of $PM_{2.5-10}$ were calculated. Figure 4.14 presents the mean ratios of the concentrations (expressed in $\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ for the traffic and background sites. This figure clearly shows that at all studied sites all carbonaceous species exhibited ratios higher than 1. Thus, $PM_{2.5}$ was the most important fraction for carbonaceous species, confirming the results shown in Table 4.10. At the sites influenced by traffic emissions, elemental carbon exhibited the highest ratios (between 4 and 4.5), indicating that traffic is mainly responsible for the emissions of this carbon in particles of smaller sizes. In general it may be concluded that traffic emissions

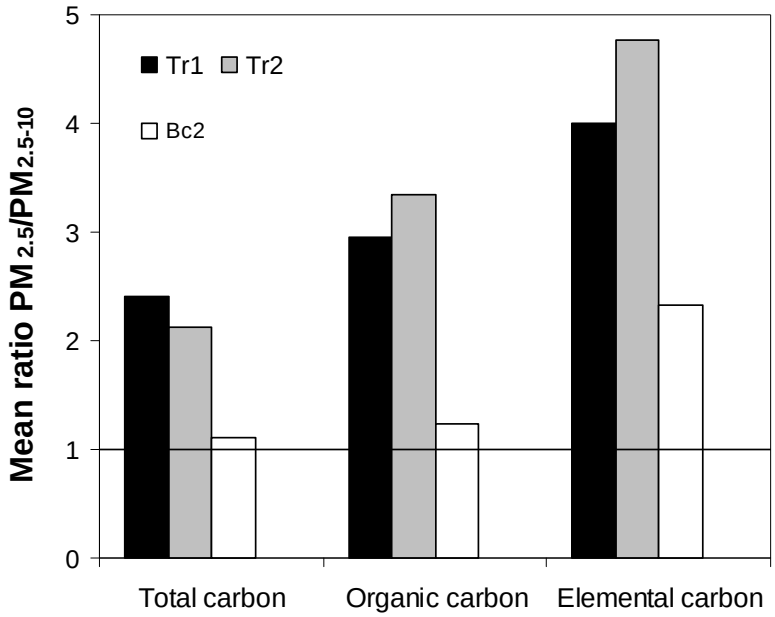


Figure 4.14 Mean ratios of total, organic and elemental carbon concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ at two traffic and one background site.

significantly increased the concentration of both $PM_{2.5}$ and PM_{10} (Table 4.10), however organic and elemental carbons were predominantly present in $PM_{2.5}$ fraction.

At the background site, organic and total carbons exhibited the lowest ratios with values only slightly higher than 1 (1.1 and 1.2) indicating that these species were also present in $PM_{2.5-10}$. It is assumed that these ratios were lower due to the presence of some natural sources that were responsible for emissions of mainly organic carbon to $PM_{2.5-10}$; as previously reported mechanical processes associated with emissions of plant spores and pollen, vegetation debris and soil organic matter produce organic particles of $PM_{2.5-10}$ fraction (Castro et al., 1999).

4.1.5 Polycyclic aromatic hydrocarbons

The concentrations of PAHs in PM_{10} and $PM_{2.5}$ samples collected at Tr_2 and Bc_2 were determined using the procedure described in Section 3.2.4. The 15 PAHs referred in Table 4.12 were detected in more than 95% of PM_{10} and $PM_{2.5}$ samples; as acenaphthylene and acenaphthene were detected in less than 10% of samples, their detailed study was not performed. The mean concentrations and other statistical parameters are also presented in Table 4.12. The results demonstrated that: i) for both PM fractions the concentrations of each PAH and the total concentration of PAHs (Σ_{PAHs}) were significantly higher at the traffic site;

Table 4.12 PAHs in PM_{10} and $PM_{2.5}$ at the traffic (Tr_2) and background (Bc_2) sites (pg m^{-3})

	Traffic site				Background site			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Naphthalene	47.7	24.2-498	44.5	12.6-105	31.0	0.350-156	24.8	0.151-83.5
Fluorene	40.1	7.33-95.2	31.4	4.41-108	-	-	-	-
Phenanthrene	486	87.4-1310	435	32.6-1080	45.3	0.232-137	41.8	0.112-128
Anthracene	768	52.9-2990	609	60.9-2440	40.9	0.0761-72.7	35.8	0.0764-66.2
Fluoranthene	256	22.9-898	223	5.41-769	44.5	0.208-110	35.1	0.141-74.3
Pyrene	587	84.6-1470	485	48.7-1260	37.5	0.0583-101	28.4	0.104-59.4
Benz[a]anthracene	689	73.1-1730	647	81.6-1720	18.4	0.282-43.4	18.2	0.0401-63.5
Chrysene	945	106-2360	882	95.8-2380	52.7	0.110-120	45.3	0.151-110
Benzo[b]fluoranthene	1410	232-3020	1370	215-2970	76.7	0.320-203	62.3	0.292-175
Benzo[k]fluoranthene	526	86.4-1220	512	73.9-1110	21.7	0.102-53.1	17.8	0.0651-44.1
Benzo[a]pyrene	953	143-2180	933	95.1-2180	31.1	0.121-66.6	25.7	0.080-61.2
Dibenz[a,h]anthracene	4240	379-9650	4220	270-10500	132	0.557-343	105	0.467-251
Benzo[ghi]perylene	1160	94.0-2500	1130	74.2-2310	31.0	0.104-78.5	26.9	0.101-71.8
Indeno[1,2,3-cd]pyrene	1370	57.4-2840	1360	59.6-2650	54.5	0.284-137	41.7	0.213-121
Dibenzo[a,l]pyrene	23.6	2.47-70.3	21.8	1.62-68.0	-	-	-	-
Σ_{PAHs}	$143x10^2$	$23.0x10^2$-$292x10^2$	$133x10^2$	$21.0x10^2$-$264x10^2$	562	2.45-$12.5x10^2$	475	1.84-$10.1x10^2$

ii) the levels of fluorene, phenanthrene, anthracene, fluoranthene, pyrene and chrysene were at the traffic site 500-1800% higher for both fractions; iii) the levels of benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenzo[a,l]pyrene were at the traffic site 1700-3600% and 2100-3900% higher for PM_{10} and $PM_{2.5}$, respectively; iv) the highest differences between concentrations of PAHs at the traffic and background sites were observed for dibenz[a,h]anthracene and benzo[ghi]perylene, being, respectively, 3100-3700% and 3900-4100% higher for PM_{10} and $PM_{2.5}$; v) the smallest differences between concentrations of PAHs at the traffic and background sites were observed for naphthalene, this difference being, respectively, 54% and 80% for PM_{10} and $PM_{2.5}$. Thus, the results clearly showed that traffic emissions strongly increased levels of PAHs in both PM_{10} and $PM_{2.5}$.

Table 4.12 also shows that lower molecular weight PAHs (2-3 rings), such as naphthalene and fluorene, corresponded to less than 1% of Σ_{PAHs} in PM_{10} and $PM_{2.5}$ at the traffic site probably because they were predominantly present in the gas phase (Lee et al., 1995). On the contrary, PAHs with high molecular weight (5-6 rings), such as benzo[b]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, occurred in considerably higher concentrations at the site influenced by traffic emissions, being primarily associated with PM (Dallarosa et al., 2008). Dibenz[a,h]anthracene was the most abundant in traffic PM_{10} and $PM_{2.5}$, with concentrations representing about 30% of Σ_{PAHs} in both fractions. This percentage was considerably higher than those of other PAHs, being followed by benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene (approximately 10%), benzo[ghi]perylene (approximately 8%), and benzo[a]pyrene and chrysene (approximately 7%).

According to several studies, (Guo et al., 2003; Dallarosa et al., 2008; Wang et al., 2008) those PAHs (dibenz[a,h]anthracene, benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, benzo[a]pyrene and chrysene) are indicators of traffic emissions, confirming that traffic was the major source of PM pollution at the selected traffic site.

The weekday and weekend mean concentrations of PAHs in PM_{10} and $PM_{2.5}$ at the traffic site are shown in Figure 4.15.

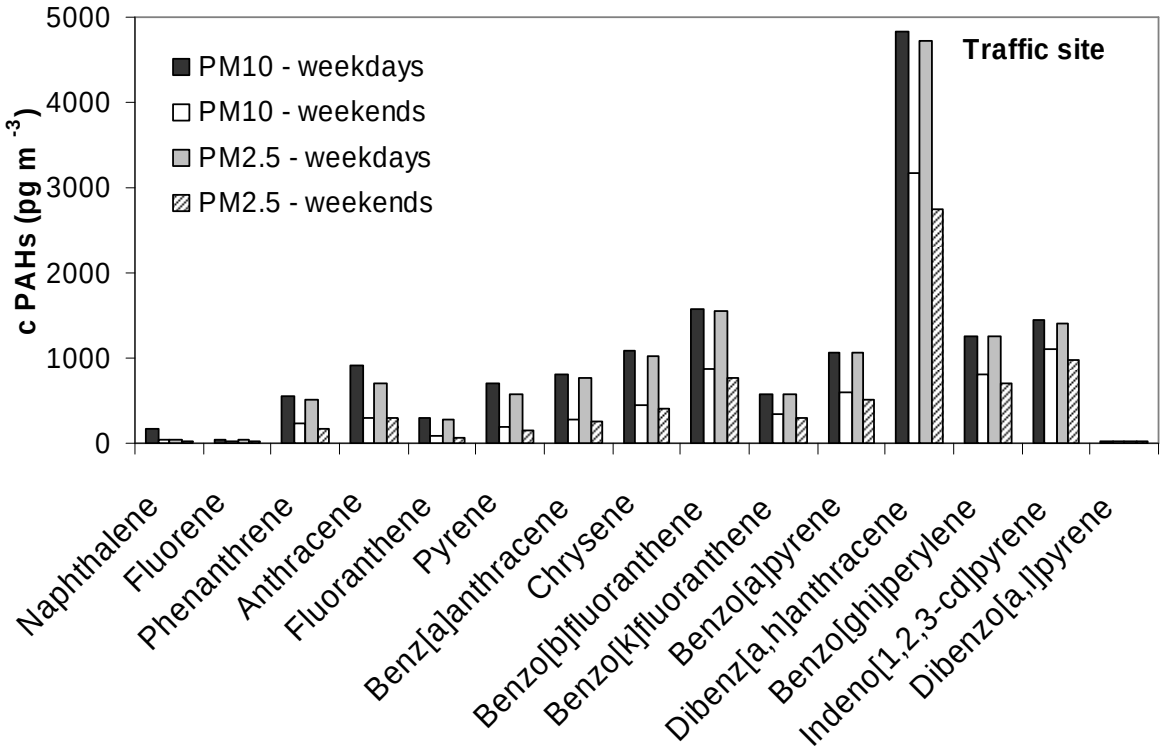


Figure 4.15 Weekday and weekend mean concentrations of PAHs in PM_{10} and $PM_{2.5}$ at the traffic site.

It can be clearly observed that concentrations of all PAHs in both PM differed significantly between the weekdays and weekends. Corresponding with the traffic patterns, concentrations of PAHs were much higher during weekdays, the highest differences being observed for benzo[b]fluoranthene and dibenz[a,h]anthracene; as these compounds are indicators of traffic emissions, the obtained results clearly confirm the influence of traffic emissions on composition of PAHs.

At the background site (Figure 4.16) no tendency was observed for the differences of PAH concentrations for both PM fractions, according to the absence of traffic influence at the background site.

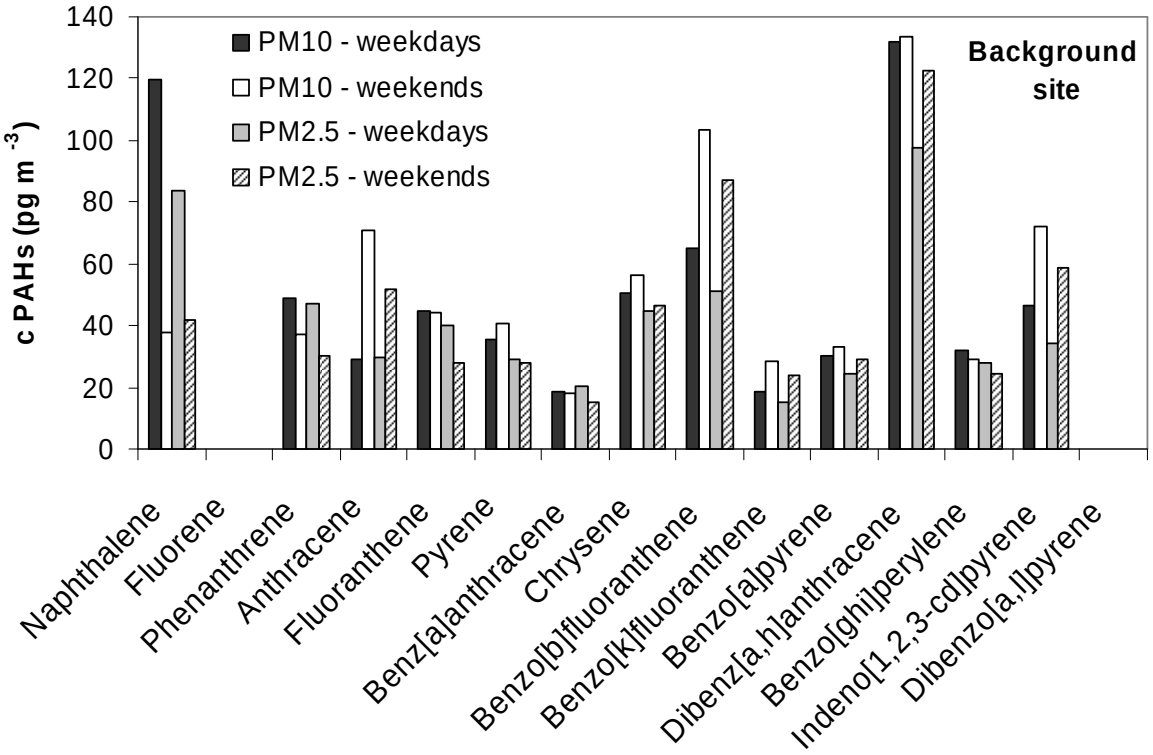


Figure 4.16 Weekday and weekend mean concentrations of PAHs in PM_{10} and $PM_{2.5}$ at the background site.

Previous studies considered the concentration ratios of several PAHs to identify their emission sources (Guo et al., 2003; Tsapakis et al., 2002); the ratio of benzo[ghi]perylene/benzo[a]pyrene has been used as an indicator of traffic emissions (Rehwagen et al., 2005; Nielsen et al., 1996). Table 4.13 presents the above mentioned ratio for the traffic and background sites. At the traffic site the benzo[ghi]perylene/benzo[a]pyrene ratios were twice higher than at the background one. Table 4.13 also shows that both traffic PM fractions exhibited similar values of benzo[ghi]perylene/benzo[a]pyrene ratios, agreeing with previous studies (Kakimoto et al., 2002), and confirming that traffic emissions were the major source of PM at the selected traffic site. It is however important to remark that benzo[ghi]perylene/benzo[a]pyrene ratios were lower than those published by Rehwagen et al. (2005), probably due to specific behaviours.

Table 4.13 Ratios of selected PAHs at the traffic and background sites

Site	$\frac{\text{Benzo[ghi]perylene}}{\text{Benzo[a]pyrene}}$				$\frac{\text{Benzo[ghi]perylene}}{\text{Indeno[1,2,3-cd]pyrene}}$			
	PM_{10}	SD	$PM_{2.5}$	SD	PM_{10}	SD	$PM_{2.5}$	SD
Traffic	1.49	0.24	1.41	0.12	1.28	0.31	1.21	0.27
Background	0.88	0.21	0.81	0.20	0.51	0.15	0.51	0.16

Other authors (Li and Kamens, 1993) assessed benzo[ghi]perylene/indeno[1,2,3-cd]pyrene ratio to distinguish the emissions from different type of engines (1.1-1.2 ratios are associated with diesel engines, while 3.5-3.8 ratios are associated with petrol engines). Table 4.13 suggests that contribution from diesel engines was considerably stronger.

To study the concentration of PAHs associated with different sizes of PM, the concentrations of PAHs in particles of $PM_{2.5-10}$ were calculated. Figure 4.17 presents the mean ratios of the concentrations (expressed in $\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ for the traffic site and background one.

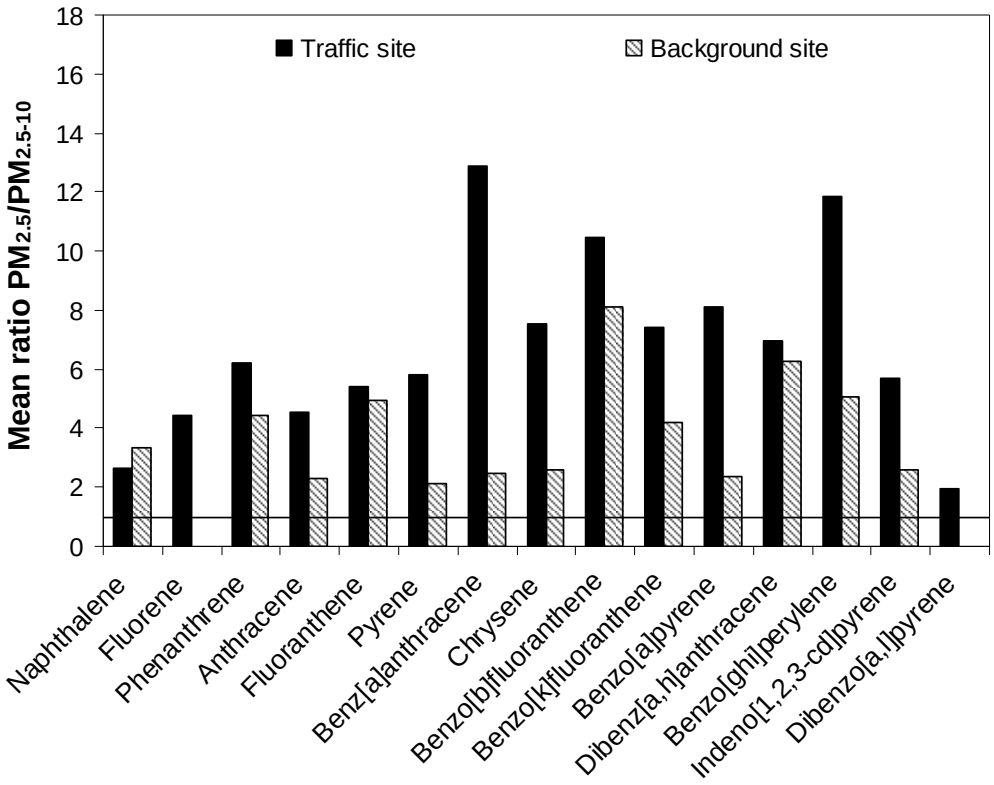


Figure 4.17 Mean ratios of PAH concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ at the traffic and background sites.

This figure clearly shows that at both sites all PAHs exhibited ratios higher than 1, being higher for the traffic site (except for naphthalene). Thus, $PM_{2.5}$ was clearly the most important fraction for PAHs, confirming the results shown in Table 4.12. At the site influenced by traffic emissions, benz[a]anthracene and high molecular weight PAHs, such as benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene and traffic markers, such as benzo[b]fluoranthene, dibenz[a,h]anthracene, benzo[a]pyrene and benzo[ghi]perylene, exhibited especially high ratios (between 7 to 13), strongly indicating that traffic is mainly

responsible for the emissions of PAHs in particles of smaller sizes. In addition it was observed that 98% and 95% of Σ_{PAHs} present in PM_{10} was in $PM_{2.5}$ at the traffic and background sites, respectively. In general it may be concluded that traffic emissions significantly increased the concentration of both $PM_{2.5}$ and PM_{10} (Figure 4.1), however PAHs were mainly present in $PM_{2.5}$ fraction. Considering the strong influence of these particles on cardiopulmonary diseases and lung cancer, this information is relevant for the development of strategies to protect the public health.

To further understand the negative impact of traffic emissions on human health, the PAHs with adverse health effects were analysed with more detail. Table 2.1 showed the carcinogenicity of all studied PAHs for different classification criteria: according to IARC, USEPA and the concept of TEF that estimates carcinogenicity relatively to benzo[a]pyrene. Out of all these PAHs, naphthalene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene were reported as carcinogenic ones (possible, probable) and therefore they are going to be analysed with more detail; dibenzo[a,l]pyrene was included in this evaluation due to its high TEF. The mean concentrations of these nine PAHs in PM_{10} and $PM_{2.5}$ are shown in Figure 4.18.

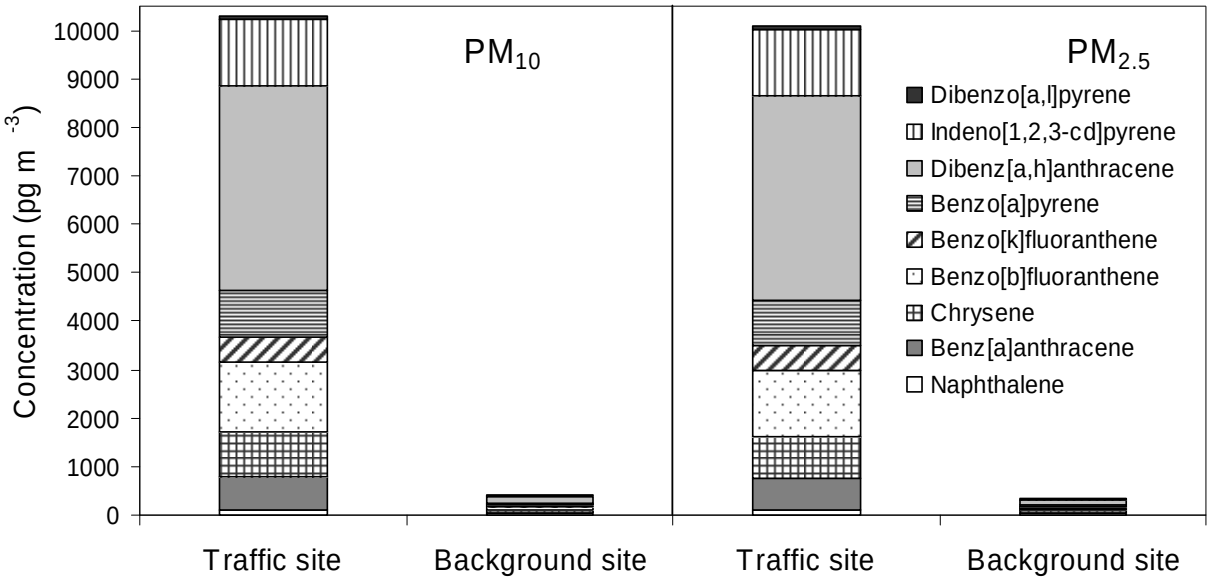


Figure 4.18 Comparison of mean concentrations of carcinogenic PAHs at the traffic and background sites.

From this figure, it is clear that at the site influenced by traffic emissions, dibenz[a,h]anthracene, with TEF of 5, was the most abundant in both PM (ranging from 379 to $96.5x10^2$ pg m^{-3} and from 270 to $105x10^2$ pg m^{-3} in PM_{10} and $PM_{2.5}$, respectively). Considering the protection of public health it is important to enhance that at both sites dibenz[a,h]anthracene exhibited the highest concentrations of all PAHs in both PM fractions, being followed by other carcinogenic compounds: benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene. Showing the strong contribution of traffic to carcinogenic content of PM, benzo[a]pyrene, the most known carcinogen, was the fourth most abundant PAH, with concentrations at the traffic site 3000% and 3500% higher in PM_{10} and $PM_{2.5}$, respectively. Dibenzo[a,l]pyrene, PAH with strong carcinogenic potency, was detected only at the site influenced by traffic emissions, showing the strong influence of traffic emissions on its presence.

The obtained results also showed that traffic emissions increased 2400% and 3000% the total concentrations of the nine carcinogenic PAHs in PM_{10} and $PM_{2.5}$, respectively. These nine carcinogenic PAHs represented 64% and 60% of Σ_{PAHs} in background PM_{10} and $PM_{2.5}$, respectively, and 68% and 74% of Σ_{PAHs} for the traffic PM_{10} and $PM_{2.5}$, respectively, indicating a strong potential risk for human health. Furthermore, the results in Table 4.12 clearly shows that for benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene the differences between traffic and background PAHs were higher for $PM_{2.5}$, suggesting that these carcinogenic PAHs predominantly occurred in $PM_{2.5}$ particles.

More detailed analysis of carcinogenic compounds was made calculating the percentage of each PAH present in PM_{10} that was contained in $PM_{2.5}$ (Table 4.14); this analysis showed that more than 95% of each carcinogenic PAH present in PM_{10} were found in $PM_{2.5}$ (with exception to naphthalene at the traffic site). As PAHs were predominantly present in $PM_{2.5}$ particles, which penetrate deep in the respiratory systems, the $PM_{2.5}$ emissions from traffic may significantly contribute to various diseases. Therefore, this information is important for the development of strategies to protect public health, namely of populations living in close vicinity of traffic emission sources.

Table 4.14 Percentage of each carcinogenic PAH present in PM_{10} that is contained in $PM_{2.5}$ at the traffic and background sites

Compound	Traffic site		Background site	
	Mean	SD	Mean	SD
	%	%	%	%
Naphthalene	85	15	95	12
Chrysene	96	7.1	94	7.3
Benz[a]anthracene	98	17	95	7.7
Benzo[b]fluoranthene	98	7.5	96	5.1
Benzo[k]fluoranthene	98	8.0	99	5.7
Benzo[a]pyrene	96	26	94	7.9
Dibenz[a,h]anthracene	99	18	97	7.9
Indeno[1,2,3-cd]pyrene	98	27	97	7.3
Dibenzo[a,l]pyrene	97	22	-	

4.1.6 Conclusions

The obtained results allowed concluding that:

- The sea salt spray plays an important role as particle source in coastal areas, influencing the concentrations and composition of PM, as well as the distribution of related elements between PM_{10} and $PM_{2.5}$ fractions; when influenced by sea salt PM_{10} concentrations increased by 46%, $PM_{2.5}/PM_{10}$ decreased by 26% and Cl in PM_{10} was 1400% higher.

- Regional transport of some anthropogenic emissions influenced particulate matter at background sites; nevertheless as the observed concentrations were very small, they could be used as reference sites for comparison of results at polluted places.

- Traffic emissions increased 370-680% PM_{10} concentrations and 360-750% $PM_{2.5}$ concentrations.

- The elements originated mostly from anthropogenic activities were predominantly present in $PM_{2.5}$ fraction; the elements mostly originated from crust predominantly occurred in the particles of $PM_{2.5-10}$. Results obtained by PIXE were consistent with those of SEM-EDS.

- At the sites influenced by traffic emissions, particle metal contents were for PM_{10} 15-4600% higher and for $PM_{2.5}$ 110-2600% higher than at the backgrounds sites; traffic emissions increased greatly the levels of metals.

- At the sites influenced by traffic emissions the levels of organic carbon were, respectively, 240-480% and 290-390% higher for PM_{10} and $PM_{2.5}$, whereas concentrations of elemental carbon increased 500-900% and 490-740% for PM_{10} and $PM_{2.5}$, respectively.

- Traffic emissions, being originated from diesel engines mainly, significantly increased PAHs in PM_{10} and $PM_{2.5}$:

    - The low molecular weight PAHs (naphthalene, fluorene, phenanthrene and anthracene) were, respectively, 54-1800% and 80-1600% higher in PM_{10} and $PM_{2.5}$.

    - PAHs with higher molecular weight (benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenzo[a,l]pyrene) reached values of 1700-3700% and 1800-4100% higher in PM_{10} and $PM_{2.5}$, respectively.

    - Carcinogenic compounds (naphthalene, chrysene benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene) and dibenzo[a,l]pyrene increased 2400% and 3000% for PM_{10} and $PM_{2.5}$, respectively; these nine compounds represented, respectively, 68% and 74% of total PAHs. These carcinogenic compounds as well as other PAHs were mainly present in $PM_{2.5}$.

4.2 Indoor Air

4.2.1 PM_{10} and $PM_{2.5}$ concentrations

To study the influence of tobacco smoke on PM_{10} and $PM_{2.5}$ particles were collected at two sites influenced by tobacco smoke (Ts_1, Ts_2) and two reference sites not influenced by

tobacco smoke (Rf_1, Rf_2), as described in Section 3.3.2. During that time the means of indoor temperatures were 24 ± 3 °C and 21 ± 4 °C at sites Ts_1 and Ts_2, respectively, and 21± 3 °C and 23 ± 3 °C at sites Rf_1 and Rf_2, respectively. The mean CO_2 levels were ranging from 680 ± 150 to 740 ± 200 ppm at sites Ts_2 and Ts_1, respectively, and from 450 ± 110 to 590 ± 100 ppm at the reference sites Rf_2 and Rf_1.

At both sites influenced by tobacco smoke PM_{10} concentrations were well correlated with $PM_{2.5}$ as the correlation coefficient square (R^2) was 0.94 (Figure 4.19), indicating that PM fractions at these sites were influenced by similar sources.

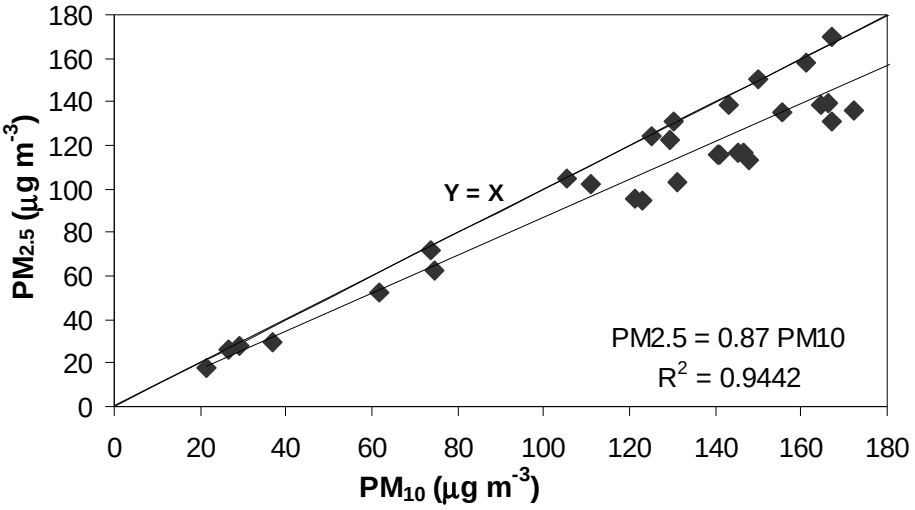


Figure 4.19 $PM_{2.5}$ and PM_{10} correlation for the sites influenced by tobacco smoke.

The means and other statistical parameters of PM fractions at the two sites influenced by tobacco smoke and at the two reference sites are summarised in Figure 4.20. At the sites influenced by tobacco smoke, PM_{10} concentrations ranged from 21.3 to 220 µg m^{-3} (mean of 107 µg m^{-3}) and from 111 to 242 µg m^{-3} (mean of 156 µg m^{-3}), the corresponding $PM_{2.5}$ concentrations ranged from 17.6 to 202 µg m^{-3} (mean of 103 µg m^{-3}) and from 95.0 to 213 µg m^{-3} (mean of 132 µg m^{-3}). The reference sites exhibited lower values of PM, ranging from 8.4 to 58.8 µg m^{-3} (mean of 29.3 µg m^{-3}) and 6.8 to 44.8 µg m^{-3} (mean of 23.6 µg m^{-3}) for PM_{10} concentrations; the corresponding $PM_{2.5}$ concentrations ranged from 6.9 to 58.2 µg m^{-3} (mean of 24.6 µg m^{-3}) and from 6.1 to 40.5 µg m^{-3} (mean of 16.9 µg m^{-3}). The statistical analysis of these results indicated that: i) as expected, PM_{10} and $PM_{2.5}$ concentrations were significantly higher at the sites influenced by tobacco smoke than at the reference ones; ii)

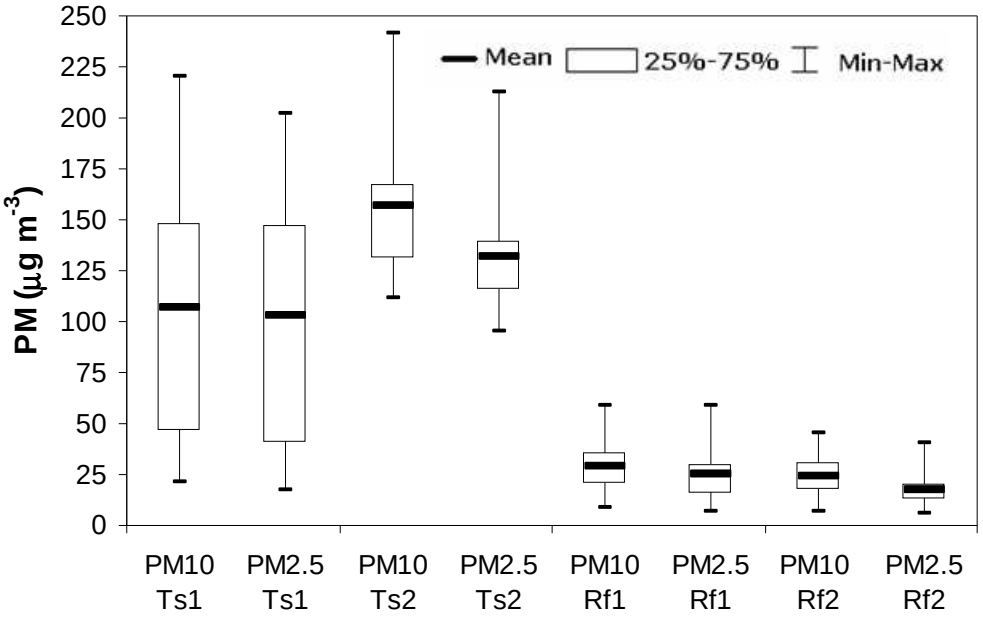


Figure 4.20 Indoor concentrations of PM_{10} and $PM_{2.5}$ measured at four sites: means, minima and maxima values, 25th and 75th percentiles.

the differences observed between PM_{10} means at sites Ts_1 and Ts_2 were statistically significant; iii) the differences observed between $PM_{2.5}$ means at sites Ts_1 and Ts_2 were not statistically significant; iv) the differences observed between PM_{10} means at sites Rf_1 and Rf_2 were statistically significant; v) the differences observed between $PM_{2.5}$ means at sites Rf_1 and Rf_2 were not statistically significant; vi) PM_{10} and $PM_{2.5}$ means were significantly different at sites Ts_2 and Rf_2 but not at sites Ts_1 and Rf_1. In general, the results showed that tobacco smoke increased concentrations 270-560% for PM_{10} and 320-680% for $PM_{2.5}$. These results allowed concluding that tobacco smoke strongly increased PM concentrations, this increase being clearly higher for $PM_{2.5}$ (Table 4.15).

Table 4.15 Concentration of $PM_{2.5}$, PM_{10} and $PM_{2.5-10}$ at the monitoring sites ($\mu g\ m^{-3}$)

	Tobacco smoke sites				Reference sites			
	Ts_1		Ts_2		Rf_1		Rf_2	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
$PM_{2.5}$	103	63.7	132	29.1	24.6	12.5	16.9	7.5
PM_{10}	107	66.0	156	31.7	29.3	13.4	23.6	9.3
$PM_{2.5-10}$	3.8	5.4	24.5	11.6	4.7	2.3	6.7	6.0

In order to study the relationship between different PM fractions, $PM_{2.5}/PM_{10}$ mass concentration ratios were also analysed (Table 4.16).

Table 4.16 Statistics for $PM_{2.5}/PM_{10}$ ratios at the monitoring sites

Site	Mean	SD	Min	Max	25^{th} percentile	Median	75^{th} percentile
Ts_1	0.95	0.07	0.81	1.00	0.93	0.98	0.99
Ts_2	0.87	0.07	0.79	1.00	0.82	0.85	0.89
Rf_1	0.86	0.10	0.68	0.99	0.80	0.88	0.94
Rf_2	0.74	0.13	0.52	1.00	0.64	0.74	0.81

The lowest $PM_{2.5}/PM_{10}$ mean ratio of 0.74 was observed at site Rf_2. This lower value was probably caused by occasional ventilation of outdoor air with higher proportion of $PM_{2.5-10}$ particles, emitted from large construction works that took place near this site during the monitoring campaign. At the other monitoring sites, the mean $PM_{2.5}/PM_{10}$ ratios ranged between 0.86 and 0.95, being the highest for site Ts_1 (smoking office). The ratios of all these three indoor ambiences were considerably higher than those previously found in this district outdoors (Section 4.1.1). High values of $PM_{2.5}/PM_{10}$ ratios indicate that indoor PM_{10} were mostly composed of $PM_{2.5}$.

The results in Table 4.16 also showed that $PM_{2.5}/PM_{10}$ ratios were higher at the smoking places (mean of 0.91) than at reference ones (mean of 0.80). As observed in Table 4.15, $PM_{2.5}$ concentrations were significantly higher (320-680%) at the sites influenced by tobacco smoke but $PM_{2.5-10}$ concentrations were much lower, and for Ts_1 even similar to non-smoking (reference) ambiences. Therefore, at the smoking places the higher $PM_{2.5}/PM_{10}$ ratios, the lower $PM_{2.5-10}$ concentrations and the much higher $PM_{2.5}$ concentrations confirmed that tobacco smoke had determinant influence on the presence of smaller particles. As particles of $PM_{2.5}$ fraction have a strong influence on cardiopulmonary diseases and lung cancer (Berico et al., 1997), this information is also relevant for the development of strategies to protect the public health.

4.2.2 Bulk elemental composition

The elements most frequently associated with tobacco smoke are Na, S, Cl, K, and Br as well as metals such as Cr, Mn, Ni, Co, Zn, As, Cd and Pb (Paoletti et al., 2006; Gemenetzis et al., 2006). The following 25 elements were determined by PIXE technique, as described in Section 3.2.1, in PM_{10} and $PM_{2.5}$ sampled at two sites influenced by tobacco smoke and at two reference sites: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cd,

I, Ba, La, Ce and Pb. The mean concentrations of elements in PM_{10} and $PM_{2.5}$ and the respective SD are presented in Table 4.17.

The obtained results showed that i) at both sites influenced by tobacco smoke the levels of Cl, K, V, Cr, Mn, Ni, Zn, As, Br, Cd, La, Ce and Pb in both fractions were significantly higher than at the reference sites; and ii) the highest levels of K, V, Cr, Mn, Ni, Zn, As, Br, Cd, and Pb in both fractions were recorded at site Ts_2 being 30-1800% higher than at the reference sites.

At site Ts_1, K and Cl were the most abundant elements in both PM fractions, accounting approximately for 63% and 62% of the total elemental concentrations (Σ_E) in PM_{10} and $PM_{2.5}$, respectively. It was also observed that elevated concentrations of K and Cl at the sites influenced by tobacco smoke were one of the major differences between the smoking and reference sites. Previous publications referred that K is associated with cigarette smoking and wood combustions (Kwangsam et al., 2004); however, considering zero-usage of fire places within the selected sites, K concentrations at Ts_1 and Ts_2 were due to tobacco smoking. As demonstrated on Figure 4.21 K concentrations were 370-1000% and 500-940% higher for PM_{10} and $PM_{2.5}$, respectively. High levels of Cl at the sites influenced by tobacco smoke were also attributed to cigarette smoking in agreement with other studies (Gemenetzis et al., 2006); at these sites Cl concentrations were 70-120% and 120-540% higher for PM_{10} and $PM_{2.5}$, respectively. Concluding, tobacco smoke influenced the compositions of both PM_{10} and $PM_{2.5}$, greatly increasing the levels of K and Cl. It is, however, important to point out that at the reference sites Rf_1 and Rf_2 where smoking was not performed, the Cl concentrations in PM_{10} were, even so, at substantial levels. The elevated concentrations of Cl in PM_{10} were at these sites probably due to the influence of outdoor air rich in Cl particles, according to the previous results (Section 4.1.2) which showed that sea salt spray strongly influenced particle composition in coastal areas.

Table 4.17 Mean concentrations of elements in PM_{10} and $PM_{2.5}$ at the monitoring sites (ng m^{-3})

	Ts_1				Ts_2				Rf_1				Rf_2			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Mg	38.6	22.3	-	-	94.0	53.7	80.5	52.1	86.2	73	36.5	26.0	31.8	14.7	-	-
Al	27.5	9.35	15.2	11.3	1170	390	383	357	199	42.4	87.9	55.0	743	397	343	187
Si	151	77.2	94.2	54.8	2070	826	594	248	210	85.8	99.2	32.3	891	517	578	296
P	-	-	-	-	81.4	33.3	20.5	13.3	34.5	21.5	16.6	6.8	23.0	10.0	10.8	6.15
S	427	173	423	194	2430	864	2170	841	630	251	536	214	617	567	524	519
Cl	1650	654	1360	683	1460	292	911	209	883	464	212	104	741	691	409	390
K	1110	890	1020	856	1950	376	1290	359	177	72.1	124	41.3	238	122	169	94.8
Ca	107	43.4	68.4	32.7	1600	523	394	149	233	105	102	43.2	462	266	231	121
Ti	5.58	1.99	2.60	1.65	53.8	16.2	14.8	6.02	8.72	3.80	4.00	1.52	12.1	7.20	5.94	3.06
V	3.95	0.58	3.48	2.76	18.7	9.28	10.2	6.42	2.06	1.36	1.83	1.15	3.66	2.32	2.71	1.94
Cr	2.23	1.94	1.43	0.94	7.83	2.33	2.83	1.81	1.04	0.40	0.76	0.27	1.95	0.87	1.20	0.65
Mn	2.85	0.91	2.39	1.16	13.2	4.72	7.04	5.16	1.43	0.63	1.11	0.36	2.16	0.84	1.93	1.05
Fe	91.8	53.4	72.4	43.5	550	172	183	64.2	109	45.3	60.4	27.2	138	95.7	63.5	35.6
Ni	2.12	1.97	1.99	1.86	7.52	3.62	6.55	3.44	1.31	0.57	1.07	0.52	1.85	1.27	1.76	0.93
Cu	5.72	3.36	4.56	2.87	17.7	5.83	10.7	6.64	42.1	35.7	33.5	26.7	27.9	27.2	23.8	15.7
Zn	63.3	41.6	53.1	46.3	106	45.0	66.2	30.0	18.0	10.5	13.9	6.38	30.2	19.2	23.3	16.5
As	103	39.8	66.2	24.8	176	61.1	94.5	58.4	-	-	-	-	-	-	-	-
Se	-	-	-	-	2.16	0.48	1.53	0.24	-	-	-	-	-	-	-	-
Br	178	93.0	152	60.4	281	73.7	247	132	157	115	91.0	54.6	138	71	13.0	4.4
Cd	9.63	8.91	7.60	5.41	64.1	37.1	32.3	10.8	-	-	-	-	-	-	-	-
I	33.8	11.7	27.1	15.0	52.5	11.1	30.8	7.94	28.8	6.83	28.6	8.11	35.8	8.20	33.1	5.17
Ba	24.9	13.8	-	-	9.58	4.13	-	-	4.10	0.58	-	-	5.43	2.73	-	-
La	27.5	8.97	26.0	22.0	15.1	6.14	4.79	1.49	-	-	-	-	-	-	-	-
Ce	32.9	23.7	26.8	28.1	31.5	12.2	18.7	8.37	-	-	-	-	-	-	-	-
Pb	14.4	9.75	12.7	6.96	14.5	5.53	8.48	3.72	5.15	1.69	4.42	1.60	6.96	4.42	6.62	3.85
Σ_E	4360	1670	3810	1840	12400	2380	6480	1430	2940	1950	1460	234	4100	1870	2490	960

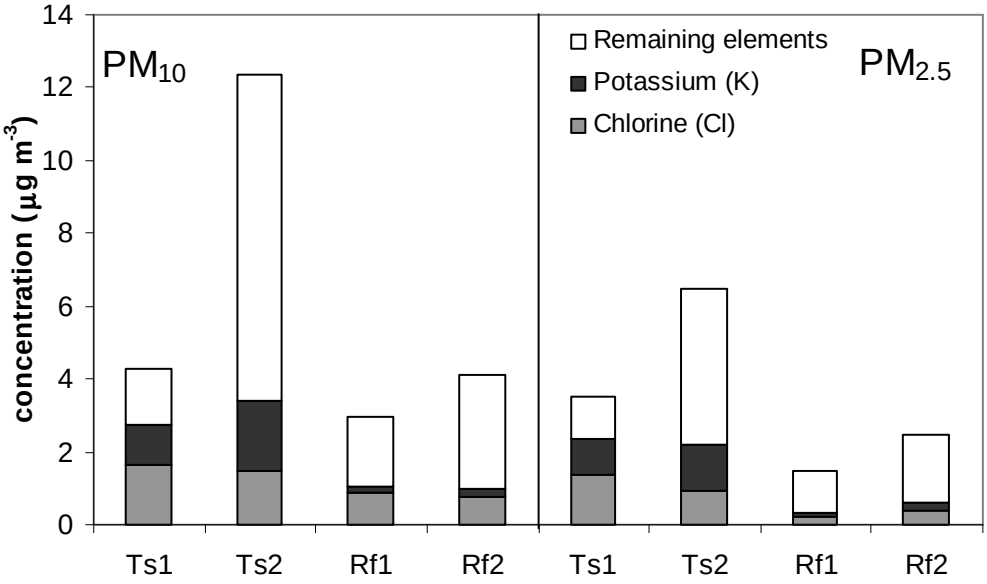


Figure 4.21 Mean concentrations of K, Cl at two sites influenced by tobacco smoke (Ts_1, Ts_2) and two references sites (Rf_1, Rf_2).

Except for K and Cl, the most abundant elements in both PM fractions at Ts_2 were Al, Si, S and Ca (Table 4.17). Presence of Al and Si in indoor ambiences commonly results from erosion of building materials or soils (Chao and Wong, 2002), spreading to indoor ambiences namely due to low-quality building isolation and air ventilation. S usually derivates from sulfurous compounds present in atmosphere or inside the building as consequence of the erosion of walls containing gypsum ($CaSO_4.2H_2O$).

The obtained results also showed that the means of total elemental concentrations (Σ_E) were significantly higher at Ts_2 than at other sites (180-320% and 70-340% for PM_{10} and $PM_{2.5}$, respectively). The characteristics of Ts_2 (high number of occupants and smoked cigarettes, and all-day cooking) justified the highest PM concentrations and consequently the higher elemental concentrations.

The concentrations of all elements in $PM_{2.5}$ versus PM_{10} were also evaluated. For the sites influenced by tobacco smoke, around 80-90% of S, Cl, K, Cr, Ni, As, Cd, and Pb present in PM_{10} were included in $PM_{2.5}$. This percentage was lower for V, Mn, Fe, Cu, Zn, I, Br and Ce (60-80%) and even lower (below 50%) for Mg, Al, Si, P, Ca and Ti. In general, at both sites influenced by tobacco smoke, the elements associated with smoking (S, Cl, K, Cr, Ni, As, Cd and Pb) were predominantly present in $PM_{2.5}$ fraction while the elements mostly

originated from building materials erosion (Mg, Al, Si, Ca and Ti) mainly occurred in the PM_{10}.

At both reference sites, more than 90% of Ni present in PM_{10} was found in $PM_{2.5}$; this percentage was lower for S, Cr, Cu, Zn, I and Pb (80-90%). Around 60-80% of K, V, Mn and Fe present in PM_{10} belonged to $PM_{2.5}$ and the percentage dropped below 50% for Mg, Al, P, Cl, Ca and Ti. At both reference sites chlorine was mainly present in PM_{10} (40% in $PM_{2.5}$). As previously referred, Cl levels at both reference sites were substantial mainly in PM_{10} fraction, probably due to $PM_{2.5-10}$ of sea salt sprays present in the outdoor air (4.1.2). Therefore, it seems reasonable to conclude that high Cl levels at reference sites could be originated from outdoor air.

To understand better the distribution of elements between both PM fractions, the elemental concentrations of $PM_{2.5-10}$ were calculated. Figure 4.22 presents the mean ratios of the elemental concentrations (expressed in $\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ for the sites influenced by tobacco smoke (Ts_1, Ts_2).

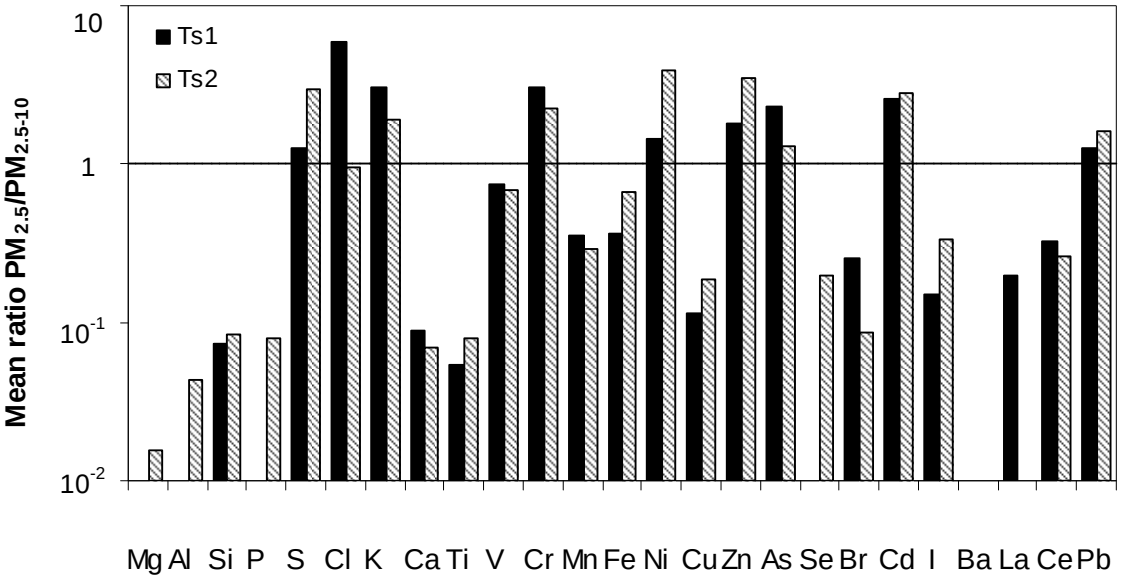


Figure 4.22 Mean ratios of elemental concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ at the sites influenced by tobacco smoke.

At Ts_1 and Ts_2, S, K, Cr, Ni, Zn, As, Cd and Pb exhibited ratios higher than 1 being the highest for Cl and Ni at Ts_1 and Ts_2, respectively. Thus, $PM_{2.5}$ was clearly the most important fraction for these elements, five of them being considered carcinogenic. Justifying the

observed values, tobacco smoke was responsible for emissions of K, Cr, Ni, Zn, As, Cd, and Pb present mostly in $PM_{2.5}$ fraction (Kwangsam et al., 2004).

At site Ts_1, Cl also exhibited ratios higher than 1, meaning that it was predominantly present in $PM_{2.5}$ fraction. At Ts_2 the ratio of Cl was 1, which means that Cl was almost equally distributed between both $PM_{2.5}$ and $PM_{2.5\text{-}10}$. While Cl in $PM_{2.5}$ was associated with tobacco smoke, the presence of Cl in $PM_{2.5\text{-}10}$ fraction indicates another source, possibly outdoor air.

At both Ts_1 and Ts_2, the ratios of Mg, Al, Si, P, Ca, Ti, V, Mn, Fe, Cu, Se, Br, I, La and Ce were lower than 1, showing that $PM_{2.5\text{-}10}$ was the most important fraction for those elements. The lowest values were observed for Mg, Al, Si and Ca which are elements usually associated with weathering of rocks or, particularly indoors, from erosion of building materials.

The mean ratios of the elemental composition in $PM_{2.5}$ versus $PM_{2.5\text{-}10}$ at the reference sites (Rf_1, Rf_2) were also evaluated (Figure 4.23).

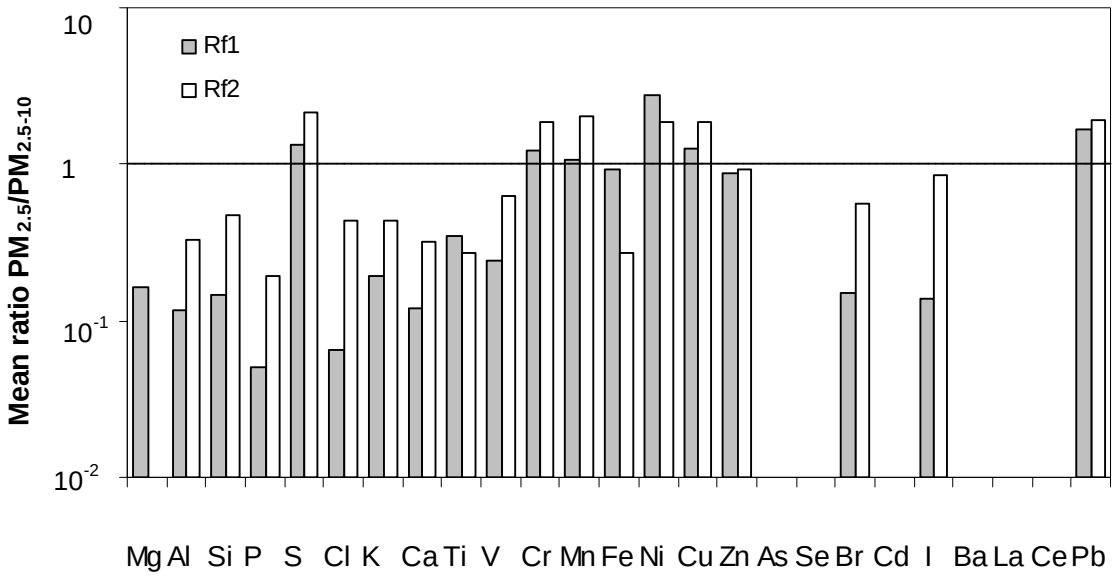


Figure 4.23 Mean ratios of elemental concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5\text{-}10}$ at the reference sites.

Results showed that the behaviour of the background sites were clearly different from those of the sites influenced by tobacco smoke. At both reference sites S, Ni and Cu exhibited the ratios higher than 1 showing that they were predominantly present in $PM_{2.5}$, while Zn exhibited ratios higher than 1 only at Rf_2. For the other elements $PM_{2.5\text{-}10}$ was the prevailing

fraction. The metallic elements in $PM_{2.5-10}$ fraction could be originated from wall paint as well as from technical equipments and devices present.

In order to evaluate the likely sources of indoor particles, enrichment factors were calculated for individual elements over the average elemental composition of the upper crust (Mason, 1958); aluminium was used as reference element in calculations, assuming that its anthropogenic contribution to atmosphere is negligible. Figure 4.24 shows the EFs calculated for PM_{10} and $PM_{2.5}$ at the sites influenced by tobacco smoke.

Figure 4.24 clearly shows that at the sites influenced by tobacco smoke the contribution of crustal sources was mainly important for typical crustal elements such as Mg, Si, Ca and Ti. Other elements (S, Cl, K, V, Cr, Ni, Cu, Zn, As, Se, Br, I, La, Ce, and Pb) were significantly enhanced by non-crustal, i.e. anthropogenic sources in both PM_{10} and $PM_{2.5}$. Between both sites slight differences were observed. While S, Cl, V, Ni, Cu, Zn, As, Br, Cd, I, La, Ce, and Pb exhibited EF greater than 10 for both PM fractions at both Ts_1 and Ts_2, K, Cr and Ni showed EFs greater than 10 for both PM at Ts_1 only; at Ts_2 these elements showed EFs greater than 10 just for $PM_{2.5}$.

Previous results (Section 4.1.2) suggested that some metallic elements may be more gathered in $PM_{2.5}$ than in PM_{10}. Figure 4.24 shows that most of the elements, namely those related to tobacco smoke (S, Cl, K, Cr, Mn, Ni, Zn, As, Cd and Pb) exhibited considerably higher EFs for $PM_{2.5}$ than for PM_{10}, confirming that tobacco smoke mainly influenced the composition of $PM_{2.5}$ fraction. At both sites influenced by tobacco smoke Br and I exhibited one of the highest EFs, showing the strong enrichment from a non-crustal source. Although Br has been used as a marker of tobacco smoke (Landsberger and Wu, 1995), in this study its concentrations were not significantly different in the smoking and reference (non-smoking) sites. Considering also that values of EFs for Br and I were similar to those observed at the reference sites (Figure 4.25), the presence of these elements could be attributed to natural indoor background. Nevertheless, despite the efforts done, the specific source of these elements was not identified.

At both reference sites (Figure 4.25) most elements in the particles were from crustal origin with EFs below 10. According to these results, Rf_1 and Rf_2 can be safely used as reference sites for comparison of results at places polluted by tobacco smoke.

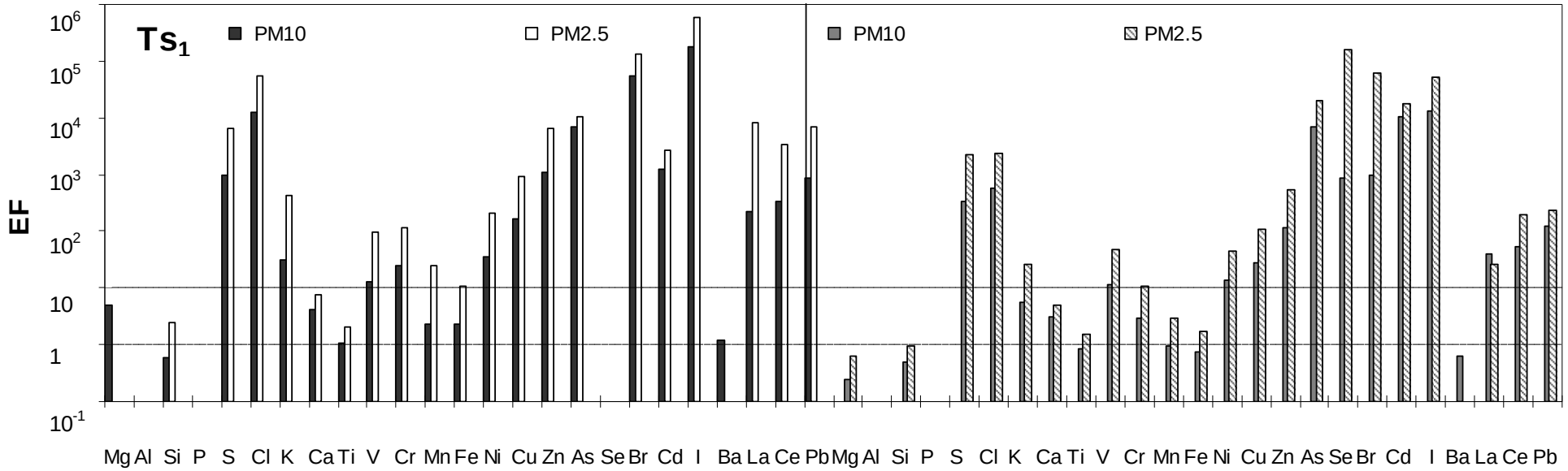


Figure 4.24 Enrichment factors for PM_{10} and $PM_{2.5}$ at two sites influenced by tobacco smoke.

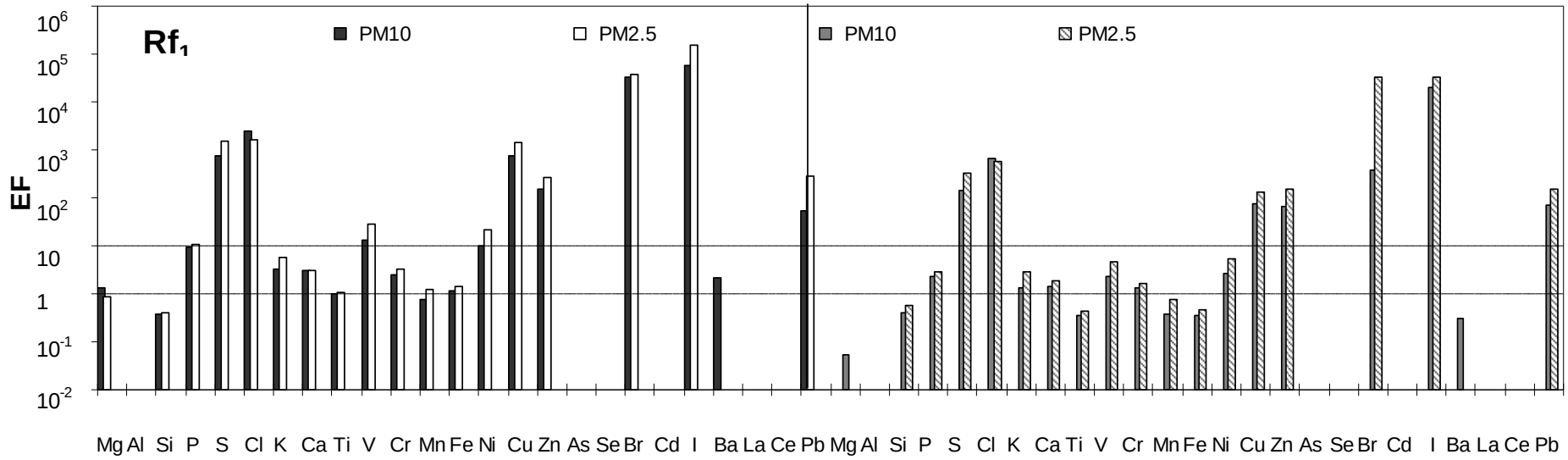


Figure 4.25 Enrichment factors for PM_{10} and $PM_{2.5}$ at two reference sites.

At both reference sites S, Cl, Cu, Zn, Br, I, and Pb were very strongly enriched with EFs>100 (Br and I exhibiting the highest levels of EFs), showing the contribution of some non-crustal sources. As previously mentioned S could be related to sulfurous compounds present in atmosphere and to building erosion; the metals could be originated by equipments; as previously mentioned the source of Br and I remained unknown. As concerning Cl, its presence could be attributed to some indoor sources; however, high EF values observed for PM_{10} in comparison with $PM_{2.5}$ suggest the influence of sea salt spray.

To further understand the influence of tobacco smoke on public health, the elements with adverse health effects were analysed with more detail. Previously, Cr, Ni, As, Cd and Pb were reported to be carcinogenic elements present in ETS (Smith et al., 1997; Landsberger and Wu, 1995). The mean concentrations of Cr, Ni, As, Cd and Pb in PM_{10} and $PM_{2.5}$ are shown in Figure 4.26.

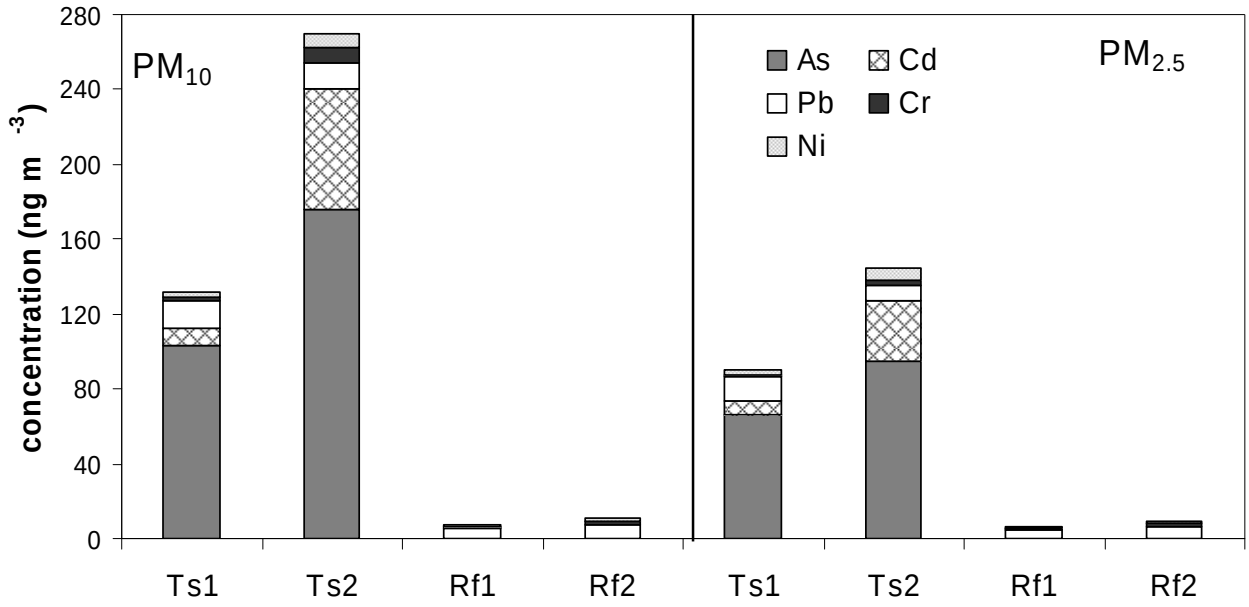


Figure 4.26 Comparison of mean concentrations of carcinogenic elements at two sites influenced by tobacco smoke (Ts_1, Ts_2) and two references sites (Rf_1, Rf_2).

From this figure, it is clear that at the sites influenced by tobacco smoke, As was the most abundant element in both PM (ranging from 103 to 176 μg m^{-3} and from 66 to 95 μg m^{-3} in PM_{10} and $PM_{2.5}$, respectively). As and Cd occurred only in PM of sites with tobacco smoke, showing its strong influence on the presence of carcinogenic elements in indoor air. Pb concentrations at these sites were 110-180% and 30-190% higher than at the reference sites

for PM_{10} and $PM_{2.5}$, respectively. Cr and Ni exhibited lower concentrations than As, Cd and Pb, mainly for the reference sites. Still, at the sites influenced by tobacco smoke, Cr and Ni concentrations in PM_{10} were 15-650% and 15-480% higher, respectively; the concentrations in $PM_{2.5}$ were 20-270% and 15-510% higher for Cr and Ni, respectively. The obtained results showed that tobacco smoke increased 1100-3500% and 840-2200% the total concentrations of five carcinogenic elements (Cr, Ni, As, Cd and Pb) in PM_{10} and $PM_{2.5}$, respectively.

4.2.3 Individual particle analysis

The individual particles of PM_{10} and $PM_{2\,5}$ were analysed for site Ts_2 (influenced by tobacco smoke) and Rf_1 (reference). The daily statistics of the respective masses are shown in Table 4.18.

Table 4.18 Daily statistics for $PM_{2.5}$ and $PM_{2.5\text{-}10}$ masses at the site influenced by tobacco smoke (Ts_2) and the reference one (Rf_1)

	Tobacco smoke site		Reference site	
	$PM_{2.5}$ μg/day	$PM_{2.5\text{-}10}$ μg/day	$PM_{2.5}$ μg/day	$PM_{2.5\text{-}10}$ μg/day
Mean	3280	640	776	184
SD	642	237	399	389
Min	2400	60	210	10
Max	5120	1020	1850	1720
25^{th} percentile	2860	580	490	35
Median	3230	690	795	90
75^{th} percentile	3490	750	963	140

A mean of 3920 μg of PM_{10} was collected per day at site Ts_2 being fractioned into $PM_{2.5}$ (daily mean: 3280 μg) and into $PM_{2.5\text{-}10}$ (daily mean: 640 μg). At the reference site Rf_1 mean of 960 μg of PM_{10} were collected per day, being fractioned into $PM_{2.5}$ (daily mean: 776 μg) and into $PM_{2.5\text{-}10}$ (daily mean: 184 μg). Confirming the previous results (Section 4.2.1) at both sites PM_{10} was mainly composed by $PM_{2.5}$. In general these results showed that tobacco smoke increased 320% $PM_{2.5}$ and 250% $PM_{2.5\text{-}10}$ masses.

In all analysed $PM_{2.5}$ and $PM_{2.5\text{-}10}$ samples collected at sites Ts_2 and Rf_1 the following 20 elements were determined by SEM-EDS analysis, as described in Section 3.3.4: C, Na, Mg, Al, Si, P, S, Cl, F, K, Ca, Mn, Fe, Cu, Zn, Pb, Ti, Cr, V, and Ni. Carbon and fluorine were

present in the filter substrate and as previously their presences in particles were not considered (Section 4.2.2). However, as carbon is an important component of tobacco particles, it was important to study it in PM. Considering the occurrence of carbon in both particles and filter substrate, a specific approach was here used: if both carbon and fluorine were determined in a spectrum of a particle, they were not further considered assuming that these elements resulted mainly from the filter substrate; if carbon was detected in a particle spectrum whereas fluorine was not, such occurrence was attributed to the presence of carbon in the respective particle.

In order to study the influence of tobacco smoke on PM, the SEM-EDS analysis of individual particles in $PM_{2.5}$ and $PM_{2.5-10}$ was performed to evaluate their chemical compositions and morphological parameters. CA method was applied to 4000 particles allowing the identification of the main groups of particles according to their similar chemical compositions and morphological characteristics, aiming the identification of the respective emission sources.

Figure 4.27 shows the main identified groups of particles in $PM_{2.5}$ at the reference site Rf_1; the means of morphological parameters of these groups are presented in Table 4.19.

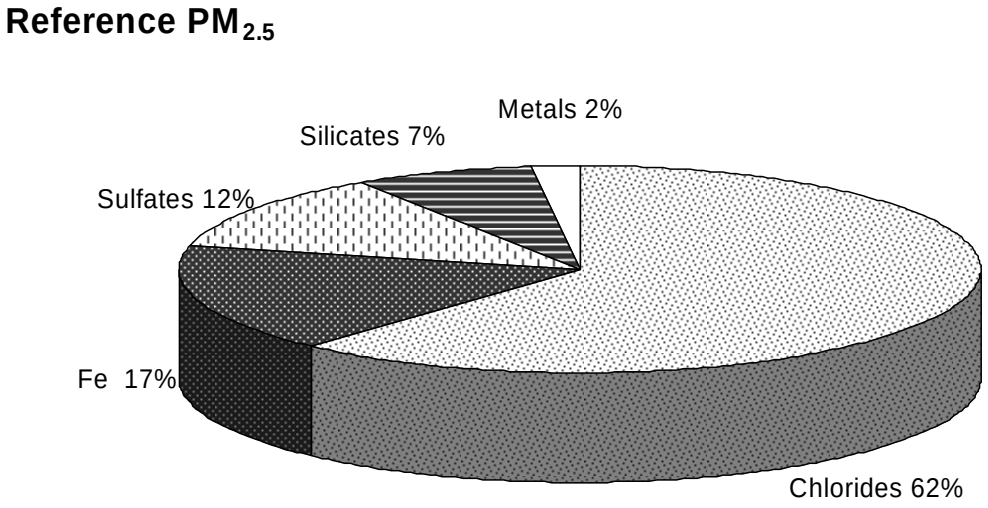


Figure 4.27 Main groups of particles in $PM_{2.5}$ identified by CA method at the reference site (Rf_1).

Table 4.19 Means of abundances and morphological parameters of particles identified in $PM_{2.5}$ at the reference site (Rf_1)

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Chlorides	62	3.18	1.41	1.52	2.21	1.86	1.51	2.18	1.89	5.82	1.48
Fe oxides and alloys	17	1.37	1.55	0.99	1.48	1.24	0.83	1.34	1.12	3.23	1.01
Sulfates	12	1.95	1.59	1.16	1.87	1.51	1.21	1.87	1.58	4.89	1.34
Silicates	7	1.97	1.59	1.12	1.78	1.45	1.13	1.78	1.49	4.52	1.32
Metal-rich s	2	0.19	1.46	0.37	0.57	0.47	0.27	0.45	0.38	1.02	1.01

The most abundant group of this fraction was of chlorides (62%), which could be originated from various indoor sources, such as cooking fumes (Wei See and Balasubramanian, 2008), cleaning works and products (Sulaiman et al., 2005), and from dust released from building materials (Abdel Hameed et al., 2004); in coastal cities indoor chlorides also result from penetration of outdoor particles originated from sea salt sprays (Sulaiman et al., 2005). The second most abundant group of $PM_{2.5}$ were particles constituted by Fe oxides and alloys (17%). They were rich in Fe (in the form of oxides and alloys), accompanied by other metals such as Cu, Zn, Pb, Ni and Cr. As previously shown (Section 4.1.3), these particles are common in Oporto urban air, especially in $PM_{2.5}$, as they can be originated from traffic emissions (Moreno et al., 2003); indoor they appeared due to contribution of outdoor emissions. The third most abundant group of particles in $PM_{2.5}$ was constituted by sulfates (12%) containing Na and K; these particles were sea-related sodium and potassium sulfates that also resulted from contribution of outdoor particles. The remaining groups of particles in reference $PM_{2.5}$ showed considerably lower abundances: silicates (7%) originated most likely from other erosions of building materials, and metal-rich particles (2%) with high proportions of Cu, and Zn probably originated from various equipments present in the monitoring place.

Five groups of particles were identified in $PM_{2.5\text{-}10}$ fraction at the reference site Rf_1 (Figure 4.28); the means of morphological parameters of these groups are shown in Table 4.20.

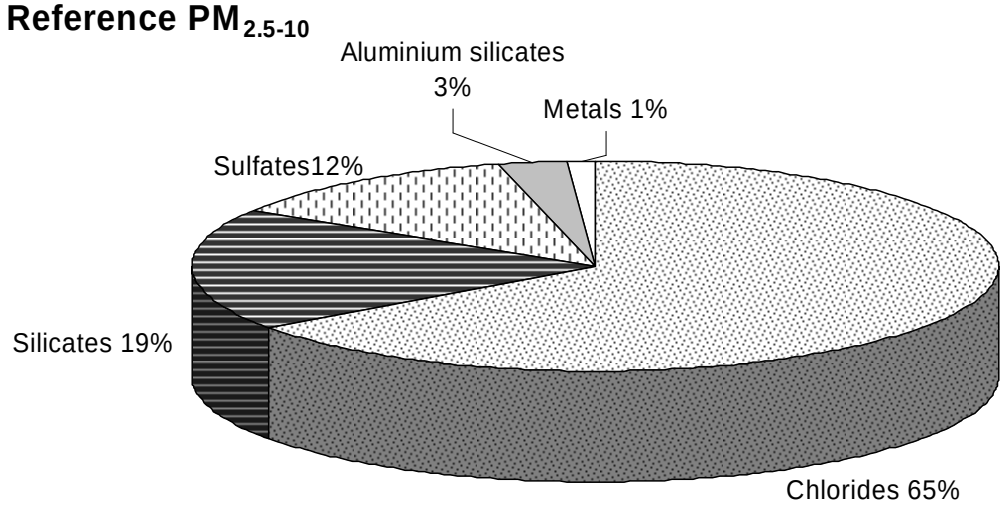


Figure 4.28 Main groups of particles in $PM_{2.5\text{-}10}$ identified by CA method at the reference (Rf_1) site.

Table 4.20 Means of abundances and morphological parameters of particles identified in $PM_{2.5-10}$ at the reference site (Rf_1)

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Chlorides	65	10.7	1.68	2.48	4.51	3.52	2.94	4.74	3.94	12.5	1.23
Silicates	19	20.8	2.09	2.99	7.47	5.19	4.21	7.80	6.26	21.1	1.83
Sulfates	12	8.88	1.90	2.45	4.49	3.41	2.77	4.88	3.97	13.0	1.55
Aluminium silicates	3	10.9	1.21	2.96	3.69	3.35	3.24	4.18	3.67	11.5	1.12
Metals	1	16.5	1.22	3.53	5.37	4.13	3.86	5.84	5.12	16.2	1.26

The most abundant group in $PM_{2.5-10}$ was of chlorides (65%), being followed by silicates (19%) resulting from building erosions and sodium and potassium sulfates (12%). Other groups of $PM_{2.5-10}$ fraction were considerably less abundant than previous three types: aluminium silicates (3%) and metals (1%). While metal particles were rich in Cu and Zn originated probably from various equipments in apartment, aluminium silicates resulted from penetration of outdoor particulates. Aluminium silicates composed mainly of Al, Si and K, and they belonged to felsic silicates (Si and Al-rich). As previously shown (Section 4.1.3), due erosion of local geological formations, these particles are commonly found in air, mainly in $PM_{2.5-10}$.

The main groups of particles identified in $PM_{2.5}$ at the site influenced by tobacco smoke (Ts_2) are shown in Figure 4.29; the morphological parameters of these groups are presented in Table 4.21. It is obvious that $PM_{2.5}$ was dominated by sulfates (34%). They were Ca sulfates that can be traced to indoor sources through erosion of building walls made from gypsum ($CaSO_4.2H_2O$) (Begonha, 1997), or due to reaction between materials composed by Ca carbonates and sulfurous compounds present in the atmosphere (Paoletti et al., 2006). The second most abundant group was composed of particles that resulted from tobacco combustion (27%). Previously, some studies showed (Thielen et al., 2008; Iskander, 1986; Al-Saleh and Saleh, 1986) that Na, S, Cl, K, and Ca were detected in tobacco, and that carbonaceous particles carrying alkaline metals, and Al, Ca and Ti were result of tobacco smoking (Paoletti et al., 2006). Accordingly, the group of particles here analysed contained mainly carbon and tracers of the mentioned metals. Other authors (Paoletti et al., 2006) reported higher abundances of carbonaceous particles from tobacco smoke; in places influenced by tobacco smoke these authors reported high percentages of other carbonaceous particles including those with sulfates and with traces of Si. It is assumed that the percentage here reported was lower because of the extremely caution procedure used for carbon analysis; as mentioned previously, carbon was considered to be present in a particle only if fluorine was not detected in the respective spectra. To ensure the quality of the results here reported, carbonaceous species in tobacco smoke PM were further analysed by other techniques, being discussed in chapter 4.2.4. The third most abundant group of particles in $PM_{2.5}$ at the site influenced by tobacco smoke were aluminium silicates (25%), rich in Si with Al and K. As subsoil of north of Portugal is made of granite rich in Al, Si and K, granite is common and affordable material that is frequently used indoors for decorations (tiles and wall facing);

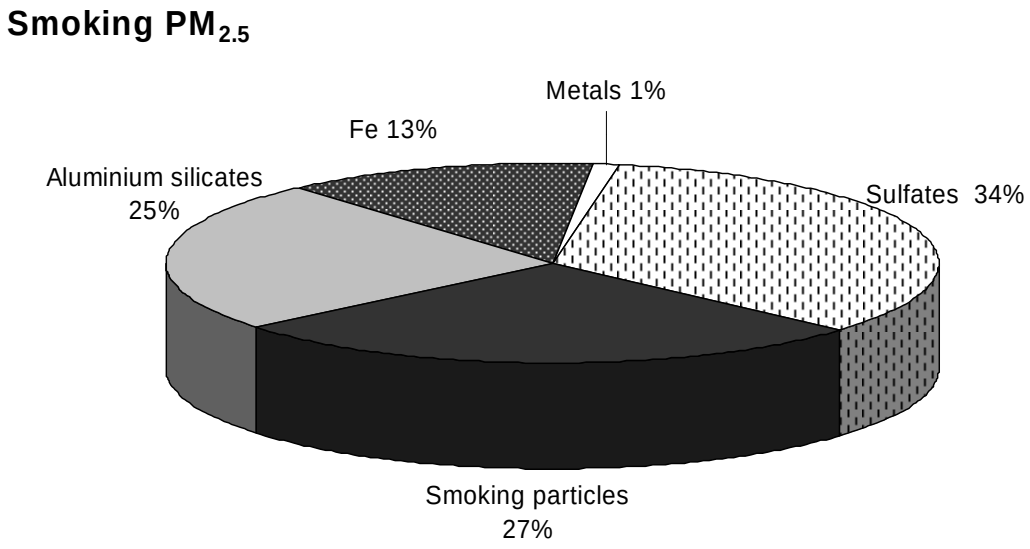


Figure 4.29 Main groups of particles in $PM_{2.5}$ identified by CA method at the site influenced by tobacco smoke (Ts_2).

it is also often used for tables and bar panels as it was the case at this site. Thus, aluminium silicates indoors could result from erosion processes of these objects. Nevertheless, site Ts_2 was highly ventilated and considering the high abundance of these particles, it is reasonable to assume that aluminium silicates also could be originated from outdoor air, being a result of soil erosions. Other groups of particles identified in $PM_{2.5}$ at the site influenced by tobacco smoke were constituted by Fe oxides and alloys (13%), also resulting from outdoor particulate emissions, mainly from traffic. Metallic particles (1%) were the least abundant group in $PM_{2.5}$ probably originating from equipments at this site.

The main groups of particles identified in $PM_{2.5-10}$ collected at the site influenced by tobacco smoke are shown at Figure 4.30; the morphological parameters of these groups are shown in Table 4.22. Sulfates clearly dominated the $PM_{2.5-10}$ fraction with abundance of 42%; aluminium silicates, rich in Al, Si and K, probably originated from outdoor natural sources forming the second most abundant group (35%). Silicates (17%) were of indoor origin resulting probably from building erosions. The last two groups of particles identified in smoking $PM_{2.5-10}$ showed considerably lower abundances: particles related from tobacco smoke (5%) and metallic particles (1%).

Table 4.21 Means of abundances and morphological parameters of particles identified in $PM_{2.5}$ at the site influenced by tobacco smoke (Ts_2)

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Sulfates	34	3.42	1.80	1.41	2.72	2.03	1.69	2.81	2.31	8.08	1.75
Tobacco smoking	27	0.71	1.56	0.64	1.13	0.88	0.77	1.16	0.99	3.34	1.44
Aluminium silicates	25	1.19	1.88	0.79	1.61	1.18	0.98	1.67	1.36	4.93	1.97
Fe oxides and alloys	13	0.93	2.25	0.65	1.53	1.05	0.83	1.58	1.25	4.58	2.22
Metals	1	1.06	1.09	0.91	1.08	1.01	0.97	1.09	1.04	3.42	1.19

Table 4.22 Means of abundances and morphological parameters of particles identified in $PM_{2.5-10}$ at the site influenced by tobacco smoke (Ts_2)

Group	Abundance	Area	Shape aspect	Physical diameter			Ferret diameter			Perimeter	Particle roundness
				(min)	(max)	(mean)	(min)	(max)	(mean)		
	%	μm^2		µm	µm	µm	µm	µm	µm	µm	µm
Sulfates	42	8.03	2.01	1.82	4.72	3.26	2.88	4.95	4.05	16.14	2.82
Aluminium silicates	35	15.9	2.00	2.53	6.20	4.30	3.64	6.44	5.21	19.81	2.45
Silicates	17	20.4	2.37	2.63	8.34	5.45	4.65	8.78	7.01	29.18	3.67
Tobacco smoking	5	5.71	3.29	1.32	4.84	3.02	1.98	5.05	3.77	14.24	4.26
Metals	1	6.97	2.02	1.53	5.73	3.26	3.10	5.95	4.71	24.53	7.45

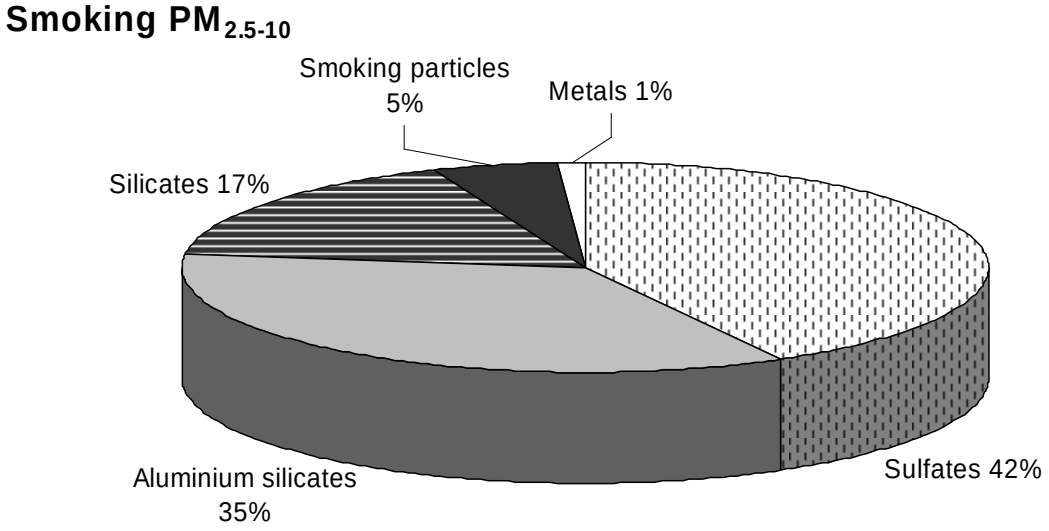


Figure 4.30 Main groups of particles in $PM_{2.5-10}$ identified by CA method at the site influenced by tobacco smoke (Ts_2).

The analysis of 4000 particles in $PM_{2.5}$ and $PM_{2.5-10}$ collected at the site influenced by tobacco smoke and at the reference one (Figure 4.27 - 4.30) allowed further comparison; Table 4.23 summarises all the groups of particles in $PM_{2.5}$ and $PM_{2.5-10}$ and their origin.

At the site influenced by tobacco smoke, particles that resulted from contribution of indoor sources showed similar percentages for both $PM_{2.5}$ and $PM_{2.5-10}$. Nevertheless, evaluating tobacco smoke specifically, it is clear that particles from this source were mainly present in $PM_{2.5}$, the percentage being 5.4 times higher than for $PM_{2.5-10}$.

The percentages of particles that resulted from contribution of outdoor emissions were at the site influenced by tobacco smoke almost identical for both PM. Outdoor particles represented 35% of $PM_{2.5-10}$ and 38% of $PM_{2.5}$ being in agreement with previous findings (Abt et al., 2000), which showed that contribution of outdoor 2-10 μm particles indoors varies between 10% and 40%; the percentage of particles smaller than 2 μm ranged from 35% to 92%.

At the reference site the majority of particles in both $PM_{2.5}$ and $PM_{2.5-10}$ were composed of chlorides with almost identical abundances for both fractions. The results in Section 4.2.2 indicate that presence of chlorides could be attributed to influence of outdoor emissions. Nevertheless, as possible indoor sources of these particles exist, chlorides were not included

Table 4.23 $PM_{2.5}$ and $PM_{2.5-10}$ at the site influenced by tobacco smoke (Ts_2) and at the reference one (Rf_1): abundances of particle main groups (%) and their respective origin

Site	PM fraction	Particle groups	Abundances (%)	Origin	Σ Origin (%)	
Tobacco smoke	$PM_{2.5}$	Sulfates	34	indoor	indoor:	62
		Tobacco smoking	27	indoor (smoking)	outdoor:	38
		Aluminium silicates	25	outdoor (natural)		
		Fe oxides and alloys c	13	outdoor (traffic)		
		Metals	1	indoor		
	$PM_{2.5-10}$	Sulfates	42	indoor	indoor:	65
		Aluminium silicates	35	outdoor (natural)	outdoor:	35
		Silicates	17	indoor		
		Tobacco smoking	5	indoor (smoking)		
		Metals	1	indoor		
Reference	$PM_{2.5}$	Chlorides	62	other	indoor:	9
		Fe oxides and alloys	17	outdoor (traffic)	outdoor:	29
		Sulfates	12	outdoor (natural)	other:	62
		Silicates	7	indoor		
		Metals	2	indoor		
	$PM_{2.5-10}$	Chlorides	65	other	indoor:	20
		Silicates	19	indoor	outdoor:	15
		Sulfates	12	outdoor (natural)	other:	65
		Aluminium silicates	3	outdoor (natural)		
		Metals	1	indoor		

in the following evaluations as their origin was not completely certain. At the reference site particles originated from indoor sources were 2.2 times higher for $PM_{2.5-10}$ fraction (20%) than for $PM_{2.5}$ (9%), showing that the respective indoor sources predominantly influenced $PM_{2.5-10}$ particles.

The contribution of particles from outdoors was at the reference site 1.9 times higher for $PM_{2.5}$ (29%) then for $PM_{2.5-10}$ fraction (15%). These results were in agreement with previous studies that showed that contribution of outdoor particles indoors generally increases with decreasing particle sizes (Geller et al., 2002). Furthermore, it was observed that outdoor natural sources contributed mainly to indoor $PM_{2.5-10}$, whereas particles of $PM_{2.5}$ fraction showed significant contribution from outdoor anthropogenic sources, namely from traffic emissions. Considering the adverse health effects of $PM_{2.5}$ particles on human health, it should be remarked that when the protection of public health is aimed, outdoor sources (i.e. traffic emissions) should be also considered.

In general the results in Table 4.23 clearly showed that the particle origins and their abundances were significantly different between both sites as PM indoors resulted from a combination of different indoor PM sources and of outdoor emissions that substantially contributed indoors.

To further understand the influence of tobacco smoke, the elements with adverse health effects, such as Cr, Ni, As, Cd, Pb, and Co were analysed with more details. Out of these the concentrations of Cr, Ni, As, Cd and Pb in $PM_{2.5}$ and $PM_{2.5-10}$ were previously determined by PIXE (Section 4.2.2). Nevertheless, SEM-EDS analysis did not reveal the presence of these metals. Although in connection with SEM, X-ray microanalysis can be performed with great spatial resolution, the relative detection limit is quite modest (~0.5%w/w). As metals are present in a cigarette only in few nanograms (Thielen et al., 2008), it is very difficult to determine their concentrations in particles of ETS, where the respective amounts of metals are distributed among a great number of particles; if these quantities of metals had been concentrated in few particles only, it would have been possible to detect them by SEM-EDS.

The results obtained by PIXE in Section 4.2.2 showed that tobacco smoke mostly influenced $PM_{2.5}$. As demonstrated in Table 4.23 this conclusion was also obtained by SEM-EDS.

4.2.4 Carbonaceous species

The concentrations of total, organic and elemental carbon in PM_{10} and $PM_{2.5}$ at two sites influenced by tobacco smoke (Ts_1, Ts_2) and at two reference sites (Rf_1, Rf_2) were determined using the procedure described in Section 3.3.3; Table 4.24 shows the means of all carbonaceous species in PM_{10} and $PM_{2.5}$ at the respective sites. The results demonstrated that: i) as expected for both PM fractions the concentrations of all carbonaceous species were significantly higher at the sites influenced by tobacco smoke than at the reference ones; ii) the highest levels for all carbonaceous species were observed at the site Ts_2; iii) the levels of total carbon at the sites influenced by tobacco smoke were, respectively, 230-410% and 230-450% higher for PM_{10} and $PM_{2.5}$; iv) the levels of elemental carbon at the sites influenced by tobacco smoke were, respectively, 15-200% and 15-180% higher for PM_{10} and $PM_{2.5}$; v) the highest differences were observed for concentrations of organic carbon, being at the sites influenced by tobacco smoke 290-500% and 300-590% higher for PM_{10} and $PM_{2.5}$, respectively. In general, these results clearly showed that tobacco smoke increased the levels of carbonaceous species of PM_{10} and $PM_{2.5}$.

The relationships between organic and elemental carbons were further evaluated. The results in Table 4.24 showed that at site Ts_1 carbon in PM_{10} and $PM_{2.5}$ was mainly composed of organic specie (91%), whereas elemental carbon contributed 9%. These percentages were slightly different at site Ts_2, where organic and elemental carbons contributed to 85% and 15% of total carbon in PM_{10} and $PM_{2.5}$, respectively. As previously mentioned, contributions of outdoor PM (originated mainly from traffic emissions) was at site Ts_2 stronger due to the often ventilation (Table 3.2), which consequently influenced the compositions of indoor PM_{10} and $PM_{2.5}$, as shown in Sections 4.2.2 and 4.2.3. Thus it is reasonable to assume that these outdoor emissions also influenced the carbonaceous composition of PM_{10} and $PM_{2.5}$ at Ts_2, increasing mainly their elemental carbon (Section 4.1.4). In general the results showed that tobacco smoke increased the concentrations of carbon in PM_{10} and $PM_{2.5}$ being mostly composed of organic species.

At both reference sites the percentages of organic carbon were similar, in PM_{10} contributing to 75% and 73% of total carbon at Rf_1 and Rf_2, respectively. Elemental carbon contributed to 25% at Rf_1; at site Rf_2 this percentage was 27% and 32% in PM_{10} and $PM_{2.5}$, respectively, being considerably higher than at the sites influenced by tobacco smoke. In general these

Table 4.24 Mean concentrations of carbonaceous species in PM_{10} and $PM_{2.5}$ at four sites ($\mu g\ m^{-3}$)

	Ts_1				Ts_2				Rf_1				Rf_2			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
Total carbon	61.9	20.1-94.5	59.7	18.0-92.1	91.2	43.2-131	81.6	23.5-121	18.9	9.8-52.3	18.1	8.7-47.0	17.9	5.6-31.2	14.9	5.9-28.4
Organic carbon	56.3	16.9-71.3	54.2	14.8-69.0	77.5	33.5-109	69.4	18.2-95.4	14.3	7.9-43.7	13.7	6.9-38.8	13.0	4.8-18.4	10.1	3.9-17.5
Elemental carbon	5.6	2.4 -8.6	5.5	2.1-7.9	13.7	8.9-29.7	12.2	4.1-25.2	4.6	1.2-7.8	4.4	1.8-8.2	4.9	1.8-12.8	4.8	1.9-10.8

results showed that at reference sites carbonaceous compositions were considerably different from those at the sites influenced by tobacco smoke.

The weight percentages (%w/w) of total, organic and elemental carbons in PM_{10} and $PM_{2.5}$ at the sites influenced by tobacco smoke (Ts_1, Ts_2) and the reference ones (Rf_1, Rf_2) were also analysed (Table 4.25).

Table 4.25 Weight percentages (%w/w) of carbonaceous species in PM_{10} and $PM_{2.5}$

	Ts_1		Ts_2		Rf_1		Rf_2	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
Total carbon	54	57	51	54	51	54	53	56
Organic carbon	50	51	41	43	40	42	36	37
Elemental carbon	4	6	10	11	11	12	17	19

At both sites Ts_1 and Ts_2, total carbon showed similar weight percentages (54-51%w/w) in PM_{10}, being similar to those in $PM_{2.5}$ (57-54%w/w), however, some differences were observed for organic and elemental carbons. At site Ts_1 organic carbon contributed to 50%(w/w) of PM_{10}, being lower (41%w/w) at Ts_2. On the contrary, elemental carbon showed higher percentages at site Ts_2 where it contributed to 10%(w/w) of PM_{10}. It is assumed that different characteristics of site Ts_2, such as number of smoked cigarettes, and ventilation (Table 3.2), justified the different percentages of organic and elemental carbon here observed.

At the reference sites the weight percentages of total carbon in PM_{10} and $PM_{2.5}$ were similar to those at the site influenced by tobacco smoke ranging from 51 to 56%(w/w). The contribution of organic carbon to PM_{10} were lower than those of smoking sites (40%w/w and 36%w/w), whereas elemental carbons contributed, respectively, 11 and 17%(w/w) at Rf_1 and Rf_2. The weight percentages observed for organic and elemental carbon in $PM_{2.5}$ were almost identical to those of PM_{10}, ranging at site Rf_1 from 12 to 42%(w/w) for elemental and organic carbon, respectively, and from 19 to 37%(w/w) at Rf_2. In general these results indicate that tobacco smoke not only increased the concentrations of carbon species in PM_{10} and $PM_{2.5}$ (Table 4.24), but it also influenced their weight percentages in both PM.

To study the concentrations of carbonaceous species associated with different sizes of PM, the concentrations of total, organic and elemental carbon in $PM_{2.5\text{-}10}$ fraction were calculated. Figure 4.31 presents the mean ratios of the concentrations in $PM_{2.5}$ versus $PM_{2.5\text{-}10}$ for two sites influenced by tobacco smoke (Ts_1, Ts_2) and at two reference sites (Rf_1, Rf_2).

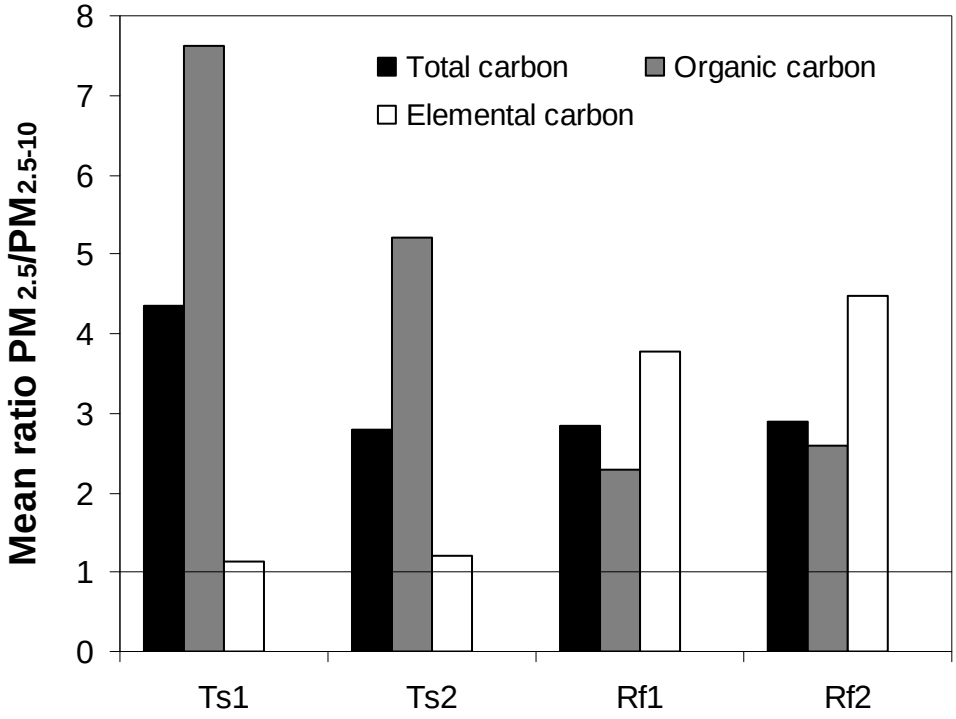


Figure 4.31 Mean ratios of total, organic and elemental carbon concentrations ($\mu g\ g^{-1}$) in $PM_{2.5}$ versus $PM_{2.5-10}$ at four sites.

This figure clearly shows that at all studied sites all carbonaceous species exhibited ratios higher than 1. Thus, $PM_{2.5}$ was the most important fraction for carbonaceous species, confirming the results shown in Table 4.24.

At the sites influenced by tobacco smoke, organic carbon exhibited the highest ratios (between 5.5 and 7.8), indicating that tobacco smoke was the main responsible for the organic carbon presence in particles of smaller sizes. It may be concluded that tobacco smoke significantly increased the concentrations of organic carbon in $PM_{2.5}$ and PM_{10} (Table 4.24), but this carbon was predominantly present in $PM_{2.5}$ fraction.

At the reference sites, elemental carbon showed the highest ratios, indicating the importance of $PM_{2.5}$ for this specie. As far as it is known there were not any specific indoor sources of elemental carbon at the reference sites, and considering the low concentrations there identified, it is reasonable to assume that PM elemental carbon resulted mainly from outdoor emissions. Supporting this assumption, elemental carbon was mainly present in $PM_{2.5}$ fraction, which penetrates indoors more commonly than $PM_{2.5-10}$.

4.2.5 Polycyclic aromatic hydrocarbons

The concentrations of PAHs in PM_{10} and $PM_{2.5}$ samples collected at one site influenced by tobacco smoke (Ts_3) and at one reference site (Rf_1) were determined using the procedure described in Section 3.3.3. The PAHs referred in Table 4.26 were detected in more than 95% of PM_{10} and $PM_{2.5}$ samples; acenaphthylene was detected in less than 10% of those samples, therefore detailed study of acenapthylene was not performed. The mean concentrations and other statistical parameters are also presented in Table 4.26. For the site influenced by tobacco smoke the results demonstrated that: i) for both PM_{10} and $PM_{2.5}$ fractions, the concentrations of each determined PAH and the total concentration of PAHs (Σ_{PAHs}) were significantly higher; ii) the levels of PAHs with 2-3 rings (naphthalene, acenaphthene, fluorene, phenanthrene, and anthracene) were 600-5500% and 700-6000% higher for PM_{10} and $PM_{2.5}$, respectively; iii) the levels of PAHs with 4 rings (fluoranthene, pyrene, benz[a]anthracene, and chrysene) were 4600-21000% and 5100-21000% higher for PM_{10} and $PM_{2.5}$, respectively; iv) PAHs with 5-6 rings (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene and indeno[1,2,3-cd] were 300-1300% and 140-1700% higher for PM_{10} and $PM_{2.5}$, respectively. Thus, the results clearly showed that tobacco smoke strongly increased levels of PAHs in both PM_{10} and $PM_{2.5}$.

At the reference site, PAHs with 5 and 6 rings, namely benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene were among the most abundant PAHs. Their concentrations were comparable to those found for non-smoking reference indoor conditions in Greece (Dermentzoglou et al., 2003). Dibenz[a,h]anthracene (carcinogenic potency approximately 5 times higher than benzo[a]pyrene) was the most abundant PAH at the reference site for both PM (Table 4.26), and its concentrations were considerably higher than those found elsewhere (Dermentzoglou et al., 2003). In addition it was observed that concentrations of dibenz[a,h]anthracene at the reference site were much higher than those at the site influenced by tobacco smoke (48% and 46% higher for PM_{10} and $PM_{2.5}$, respectively). Similar trend was observed for dibenzo[a,l]pyrene, a highly carcinogenic PAH with potency two orders of magnitude higher than benzo[a]pyrene; despite its recorded existence in tobacco smoke particulate phase (Smith et al., 2003), dibenzo[a,l]pyrene was absent at the site influenced by smoking, whereas it was found at the reference site, nevertheless being the least abundant PAH. For this period, the outdoor concentrations of dibenzo[a,l]pyrene in PM ranged between $1.6x10^{-3}$ and $70x10^{-3}$

Table 4.26 PAHs in PM_{10} and $PM_{2.5}$ at the site influenced by tobacco smoke (Ts_3) and at the reference one (Rf_1) (ng m^{-3})

	Tobacco smoke site				Reference site			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	Mean	Range	Mean	Range	Mean x 10^2	Range x 10^2	Mean x 10^2	Range x 10^2
Naphthalene	7.63	1.83-17.4	6.41	3.33-15.9	16.7	5.71-41.0	12.8	8.77-20.0
Acenaphthene	7.34	2.42-27.5	6.71	1.92-28.5	-	-	-	-
Fluorene	0.123	7.52-37.5 x10^{-2}	9.25x10^{-2}	0.718-28.0x10^{-2}	1.75	1.12-3.29	1.67	0.655-2.15
Phenanthrene	2.67	0.724-9.56	2.35	0.708-9.08	5.36	0.567-10.2	5.15	0.265-8.44
Anthracene	12.1	0.960-93.8	8.72	0.539-74.3	21.4	10.4-58.5	20.9	10.4-42.1
Fluoranthene	10.0	3.49-31.5	9.41	3.21-37.6	4.74	1.23-11.0	4.70	1.20-7.67
Pyrene	12.9	0.639-55.6	12.7	0.317-56.9	11.9	4.48-25.1	9.83	2.96-17.8
Benz[a]anthracene	6.71	1.24-19.9	5.41	1.15-16.4	14.3	1.17-27.4	13.0	3.47-28.0
Chrysene	19.1	3.38-63.0	18.7	3.02-70.4	22.9	2.75-44.1	20.7	65.4-41.7
Benzo[b]fluoranthene	5.56	1.34-11.9	5.15	1.28-10.1	61.5	5.09-123	58.9	12.3-118
Benzo[k]fluoranthene	1.18	0.254-1.98	1.36	0.493-2.06	28.7	1.94-49.2	27.8	3.79-46.4
Benzo[a]pyrene	8.92	1.65-23.6	8.38	1.55-23.0	64.0	3.13-115	61.2	10.7-102
Dibenz[a,h]anthracene	2.22	0.329-11.7	2.12	0.348-12.0	328	12.8-613	309	47.8-580
Benzo[ghi]perylene	5.06	1.31-13.5	4.50	0.730-11.1	84.3	2.72-160	78.6	14.3-145
Indeno[1,2,3-cd]pyrene	5.65	1.35-11.2	4.83	1.33-10.9	108	2.86-182	99.8	16.1-185
Dibenzo[a,l]pyrene					0.990	0.177-2.68	0.845	0.404-1.57
Σ_{PAHs}	101	41.0-302	97.2	39.8-293	775	71.0-1410	725	77.0-1180

ng m^{-3} (Table 4.12); dibenz[a,h]anthracene was the most abundant PAH compound in outdoor air, with concentrations between 0.3 and 10.5 ng m^{-3} (Table 4.12). These outdoor concentrations probably contributed to the presence of those compounds at the indoor reference place, due to often ventilation there performed. As outdoor PM in this area was mainly originated from traffic emissions (Section 4.1.5), it should be remarked that when the protection of human health is aimed, traffic emissions should be specifically considered.

At the site influenced by tobacco smoke PAHs with 4 rings (namely fluoranthene, pyrene and chrysene) were the most abundant compounds in both PM fractions (Table 4.26), with concentrations considerably higher than those of PAHs with 5 and 6 rings. Among the low molecular weight PAHs (2-3 rings) unusual occurrence was observed for fluorene and athracene. Due to unknown reasons, the concentrations of fluorene in both PM were at the site influenced by tobacco smoke significantly lower than other low molecular weight PAHs, being the least abundant compounds of all PAHs. On the contrary, at both sites the concentrations of anthracene showed to be considerably higher than those of PAHs with 2-3 rings (Table 4.26), being at the site influenced by tobacco smoke the third most abundant compound of all PAHs.

In order to evaluate the PAH profiles in PM, Table 4.27 presents the composition of PAHs, calculated in relation to the total amount of PAHs. It is clear that different composition profiles were obtained for both sites; however, at each site composition profiles of both PM_{10} and $PM_{2.5}$ were almost identical. At the site influenced by tobacco smoke, chrysene represented about 20% of Σ_{PAHs} in both PM (Table 4.27), which was the highest percentage, followed by pyrene (13%), fluoranthene (10%) and benzo[a]pyrene (9%). These PAHs were among the most abundant compounds in both PM (Table 4.26) and as their percentages were much higher at the site influenced by tobacco smoke than at the reference one, it was possible to conclude that tobacco smoke not only significantly increased the concentrations of PAHs in PM, but it also influenced their composition profiles. In addition it was observed that PAHs with 4 rings (fluoranthene, pyrene, benz[a]anthracene and chrysene) in PM accounted, respectively, for 49% and 7% of Σ_{PAHs} at the site influenced by tobacco smoke and at the reference one.

Table 4.27 Contribution of PAHs (%) in PM_{10} and $PM_{2.5}$ at the site influenced by tobacco smoke (Ts_3) and at the reference one (Rf_1): percentage of each compound calculated in relation to the total amount of PAHs (Σ_{PAHs})

Compound	Tobacco smoke site		Reference site	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
Naphthalene	5.9	5.9	6.1	5.2
Acenaphthylene	-	-	-	-
Acenaphthene	6.4	6.4	-	-
Fluorene	0.20	0.10	0.33	0.23
Phenanthrene	2.7	2.6	1.3	0.99
Anthracene	6.3	6.3	5.4	5.0
Fluoranthene	10	11	0.65	0.63
Pyrene	13	13	1.6	1.6
Benz[a]anthracene	6.6	6.0	1.7	1.7
Chrysene	19	19	3.4	3.2
Benzo[b]fluoranthene	6.1	6.1	8.4	8.2
Benzo[k]fluoranthene	1.4	1.6	2.7	2.8
Benzo[a]pyrene	9.0	9.4	6.3	7.3
Dibenz[a,h]anthracene	2.0	1.7	38	39
Benzo[ghi]perylene	5.6	5.0	11	11
Indeno[1,2,3-cd]pyrene	5.8	5.9	13	13
Dibenzo[a,l]pyrene	-	-	0.12	0.15

At the reference site, dibenz[a,h]anthracene compose 38% and 39% of Σ_{PAHs} for PM_{10} and $PM_{2.5}$, respectively, being significantly higher than the other PAHs, and followed by indeno[1,2,3-cd]pyrene (13%), benzo[ghi]perylene (11%) and benzo[b]fluoranthene (8%). The percentages of these compounds were similar to composition profiles of outdoor PM (Section 4.1.5); accordingly, several studies (Guo et al., 2003; Dallarosa et al., 2008; Wang et al., 2008) stated that these four compounds are indicators of traffic emissions, their high occurrence identifying traffic as the major PM source. Thus, it is possible to suggest that PM at the reference site was strongly influenced by outdoor PM. In addition to that it was observed that high molecular weight PAHs (5 and 6 rings) were at the reference site the most abundant compounds, accounting for 79% and 81% of Σ_{PAHs} for PM_{10} and $PM_{2.5}$, respectively, and corresponding to concentrations of 6.75 ng m^{-3} and 6.36 ng m^{-3}, respectively. These results were consistent with previous studies (Li et al., 2005), confirming that infiltration of outdoor air is the main reason for the indoor prevalence of PAHs with high molecular weight. In comparison to these results, high molecular weight PAHs accounted at the site influenced by tobacco smoke only for 30% for both PM_{10} and $PM_{2.5}$, respectively, but

corresponded to the concentrations of 28.6 ng m^{-3} and 26.1 ng m^{-3}. According to other studies (Ohura et al, 2004; Rodgman and Perfetti, 2006), these results showed that when tobacco smoke is the predominant source of PAHs, the proportion of PAHs with higher molecular weight is lower compared to one of lower molecular weight; nevertheless, it is important to enhance that despite the lower proportions of high molecular weight compounds at the site influenced by tobacco smoke, their concentrations in PM_{10} and $PM_{2.5}$ were, respectively, 320% and 310% higher than at the reference site.

To study the concentrations of PAHs associated with PM of different sizes, the concentrations PAHs in $PM_{2.5-10}$ were calculated. Figure 4.32 presents the mean ratios of the concentrations (expressed in μg g^{-1}) in $PM_{2.5}$ versus $PM_{2.5-10}$ for the site influenced by tobacco smoke and for the reference one.

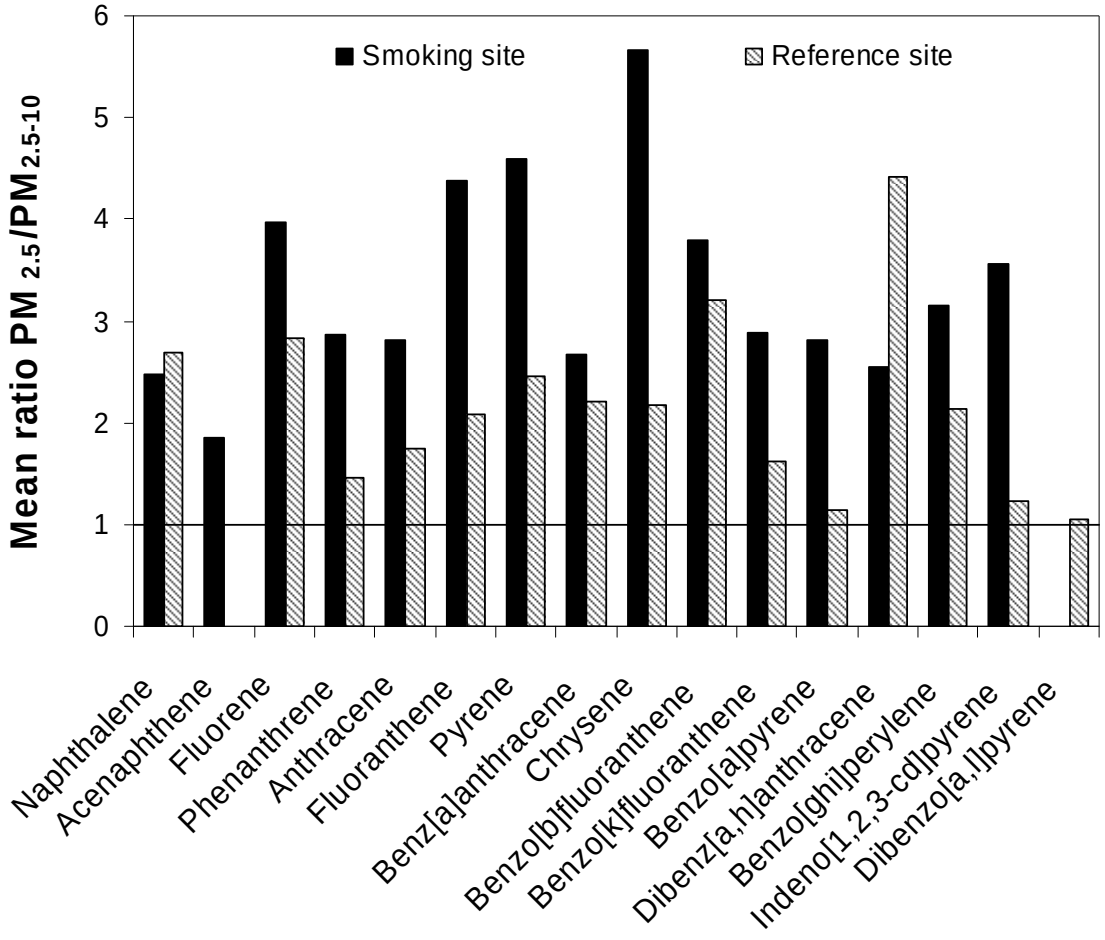


Figure 4.32 Mean ratios of PAH concentrations (μg g^{-1}) in $PM_{2.5}$ versus $PM_{2.5-10}$ at the site influenced by tobacco smoke (Ts_3) and at the reference one (Rf_1).

This figure clearly shows that at both sites all PAHs exhibited ratios higher than 1, the highest being observed for the site influenced by tobacco smoke (except for naphthalene and dibenz[a,h]anthracene). Thus, $PM_{2.5}$ was clearly the most important fraction for PAHs, confirming the results shown in Table 4.26. In addition it was observed that 96% and 94% of Σ_{PAHs} present in PM_{10} was in $PM_{2.5}$ at the site influenced by smoke and at the reference one, respectively. In general, it may be concluded that tobacco smoke significantly increased the concentrations of both PM fractions (Section 4.1.1), however PAHs were mainly present in $PM_{2.5}$, thus confirming the previous findings (Kavouras et al., 1998).

To further understand the negative impact of tobacco smoke emissions on human health, the carcinogenic PAHs were analysed with more detail. As previously mentioned, among all the PAHs analysed, naphthalene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene were reported as carcinogenic ones (possible, probable) and therefore they were further analysed with more detail; dibenzo[a,l]pyrene was also included in this evaluation due to its high TEF. The mean concentrations of these nine PAHs in PM_{10} and $PM_{2.5}$ are shown in Figure 4.33.

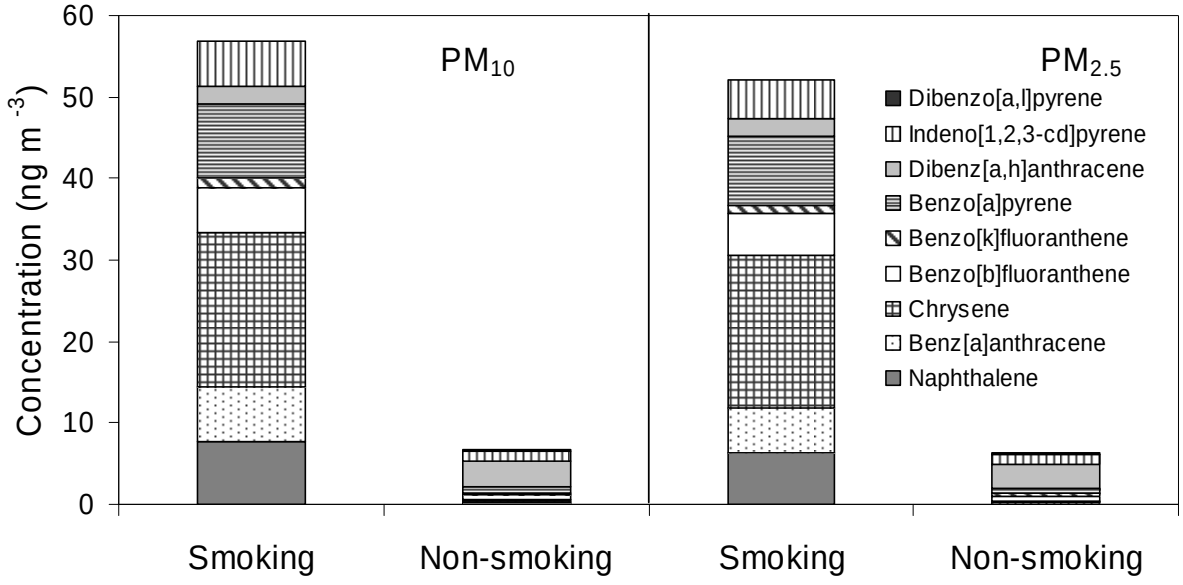


Figure 4.33 Comparison of mean concentrations of carcinogenic PAHs at the site influenced by tobacco smoke (Ts_3) and at the reference one (Rf_1).

From this figure, it is clear that at the site influenced by tobacco smoke, chrysene was the most abundant compound in both PM (ranging from 3.38 to 63.0 ng m^{-3} and from 3.02 to 70.4 ng m^{-3} in PM_{10} and $PM_{2.5}$, respectively). Considering the protection of public health it is

important to enhance that at the site influenced by tobacco smoke chrysene also exhibited the highest concentrations of all PAHs in both PM fractions, being followed by benzo[a]pyrene, (the most known carcinogen with concentrations 1300% higher in PM_{10} and $PM_{2.5}$), naphthalene and benz[a]anthracene. The lowest concentrations at the site influenced by tobacco smoke were observed for benzo[b]fluoranthene and dibenz[a,h]anthracene, but it is important to enhance that although dibenz[a,h]anthracene occurred in low concentrations, due to its high TEF the relative contribution to carcinogenic potential is high. At the non-smoking (reference) site, dibenz[a,h]anthracene with TEF of 5 was the most abundant in both PM (ranging from 0.128 to 6.13 ng m^{-3} and from 0.478 to 5.80 ng m^{-3} in PM_{10} and $PM_{2.5}$, respectively); at the reference site, dibenz[a,h]anthracene also exhibited the highest concentrations of all PAHs in both PM fractions, with mean concentrations 48% and 46% higher than at the site influenced by tobacco smoke for PM_{10} and $PM_{2.5}$, respectively. This means that even at the reference site, very harmful PAHs are present in breathable particles. As previously mentioned, dibenz[a,h]anthracene is an indicator of traffic emissions, confirming that the reference site was strongly influenced by outdoor PM.

More detailed analysis of carcinogenic compounds was made calculating the percentage of each carcinogenic PAH present in PM_{10} that was contained in $PM_{2.5}$ (Table 4.28); the results showed that at least 88% of each carcinogenic PAH present in PM_{10} was found in $PM_{2.5}$.

Table 4.28 Percentage of each carcinogenic PAH present in PM_{10} that is contained in $PM_{2.5}$, at the site influenced by tobacco smoke (Ts_3) and at the reference one (Rf_1)

Compound	Smoking site		Reference site	
		SD		SD
	%	%	%	%
Naphthalene	88	13	95	12
Chrysene	92	12	89	7.9
Benz[a]anthracene	95	9.3	91	11
Benzo[b]fluoranthene	96	12	90	10
Benzo[k]fluoranthene	94	6.1	90	7.3
Benzo[a]pyrene	95	9.8	91	8.8
Dibenz[a,h]anthracene	91	15	98	7.9
Indeno[1,2,3-cd]pyrene	90	8.1	90	10
Dibenzo[a,l]pyrene	-	-	91	7.3

Furthermore, it was observed that nine carcinogenic PAHs represented 80% and 81% of Σ_{PAHs} in reference PM_{10} and $PM_{2.5}$, respectively, and 56% and 55% of Σ_{PAHs} for the PM_{10} and $PM_{2.5}$

at the site influenced by tobacco smoke, respectively. Despite the lower proportions of the carcinogenic elements at the site influenced by smoking, the total concentrations of those carcinogenic PAHs were 780% and 770% higher in PM_{10} and $PM_{2.5}$, respectively, indicating the strong potential risk of tobacco smoke for human health.

4.2.6 Conclusions

The obtained results allowed concluding that:

- Tobacco smoke strongly increased PM concentrations, this increase being higher for particles of smaller sizes: 270-560% for PM_{10} and 320-680% for $PM_{2.5}$.
- Tobacco smoke increased the levels of K, V, Cr, Mn, Ni, Zn, As, Br, Cd, and Pb in PM_{10} and $PM_{2.5}$ by 30-1800%.
- Tobacco smoke increased the total concentrations of five carcinogenic elements (Cr, Ni, As, Cd and Pb) by 1100-3500% for PM_{10} and 840-2200% for $PM_{2.5}$, respectively:
    - Cr concentrations were 15-650% and 20-270% higher in PM_{10} and $PM_{2.5}$, respectively.
    - Ni concentrations were 15-480% and 15-510% higher in PM_{10} and $PM_{2.5}$, respectively.
    - Pb concentrations were 110-180% and 30-190% higher than at the reference sites for PM_{10} and $PM_{2.5}$, respectively.
    - As and Cd occurred only in PM of sites influenced by tobacco smoke.
- The carcinogenic elements as well as other elements associated with tobacco smoke (S, K, Zn) were predominantly present in $PM_{2.5}$ fraction; the elements mostly originated from building erosion (Mg, Al, Si, Ca and Ti) predominantly occurred in $PM_{2.5-10}$.
- Tobacco smoke increased the carbonaceous species in PM_{10} and $PM_{2.5}$:
    - Concentrations of total carbon were 230-410% and 230-450% higher in PM_{10} and $PM_{2.5}$, respectively.

- Concentrations of elemental carbon were 15-200% and 15-180% higher in PM_{10} and $PM_{2.5}$, respectively.

- Organic carbon concentrations were 290-500% and 300-590% higher in PM_{10} and $PM_{2.5}$, respectively.

- Tobacco smoke increased the concentrations and distributions of PAHs in PM_{10} and $PM_{2.5}$:

  - PAHs with 2-3 rings were, respectively, 600-5500% and 700-6000% higher for PM_{10} and $PM_{2.5}$.

  - PAHs with 4 rings, namely fluoranthene, pyrene, and chrysene, were, respectively, 4600-21000% and 5100-21000% higher for PM_{10} and $PM_{2.5}$.

  - PAHs with 5-6 rings were 300-1300% and 140-1700% higher for PM_{10} and $PM_{2.5}$, respectively.

  - Carcinogenic PAHs (naphthalene, chrysene benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene) and dibenzo[a,l]pyrene were 780% and 770% higher for PM_{10} and $PM_{2.5}$, respectively:

    - At the site influenced by tobacco smoke chrysene was the most abundant compound of all PAHs in PM_{10} and $PM_{2.5}$, being followed by benzo[a]pyrene (the most known carcinogen with concentrations 1300% in PM_{10} and $PM_{2.5}$), naphthalene and benz[a]anthracene.

    - At reference (non-smoking) site dibenz[a,h]anthracene (indicator of traffic emissions with high carcinogenic potency) was the most abundant PAH in both PM, with concentrations about 50% higher than at the site influenced by tobacco smoke.

    - Even at the reference site carcinogenic PAHs were present in PM_{10} and $PM_{2.5}$, originated from traffic emissions.

- Carcinogenic PAHs represented 56% and 55% of total PAHs for the PM_{10} and $PM_{2.5}$ at the site influenced by tobacco smoke, respectively.
- Carcinogenic PAHs represented 80% and 81% of total PAHs in reference PM_{10} and $PM_{2.5}$, respectively.

o The carcinogenic compounds as well as other PAHs were mainly present in $PM_{2.5}$ fraction.

4.3 Indoor versus outdoor air

4.3.1 PM_{10} and $PM_{2.5}$ concentrations

The results in Section 4.2 suggest that indoor PM_{10} and $PM_{2.5}$ were influenced by outdoor emissions. Therefore, the relationships between indoor and outdoor PM are discussed in this section with more details. The specific comparisons were made between outdoor PM influenced by traffic emissions (site Tr_2) and indoor PM, with and without influence of tobacco smoke (sites Ts_3 and Rf_1). Table 4.29 presents $PM_{2.5}$ and PM_{10} concentrations measured at the respective sites.

Table 4.29 $PM_{2.5}$ and $PM_{2.5-10}$ at site Tr_2 (influenced by traffic emissions), Ts_3 (influenced by tobacco smoke) and Rf_1 (reference i.e. non-smoking) ($\mu g\ m^{-3}$)

Site	$PM_{2.5}$		$PM_{2.5-10}$		I/O	I/O
	mean	range	mean	range	$PM_{2.5}$	$PM_{2.5-10}$
Tr_2	28.7	13.2-52.8	14.0	4.3-35.3	-	-
Rf_1	23.3	9.6-42.5	4.6	0.7-9.8	0.82	0.33
Ts_3	190	88.1-442	14.4	1.9-55.1	6.6	1.0

The values in Table 4.29 show that concentrations of indoor $PM_{2.5}$ at the reference (non-smoking) site were similar to those measured outdoors. Regarding the $PM_{2.5-10}$, indoor concentrations were 200% lower than those outdoors. The contributions of outdoor PM emissions were further analysed using ratio (I/O) between indoor and outdoor concentrations of particles. This ratio gives an indication whether particles found indoors are the result of indoor origin; in the absence of indoor sources, the ratio will be less than or equal to 1, whereas for ratio higher than 1 an indoor source of PM exists. The means of I/O ratios are also presented in Table 4.29 showing that at the reference site values of 0.82 and 0.33 were

observed for $PM_{2.5}$ and $PM_{2.5-10}$, respectively. These values showed that there was not any significant indoor source of PM at the respective site, indicating that indoor PM_{10} and $PM_{2.5}$ resulted from outdoors, representing a "background contribution" of outdoor particles to indoor PM.

When influenced by tobacco smoke, indoor $PM_{2.5}$ concentrations were 560% higher than those measured outdoors, whereas no differences were observed for $PM_{2.5-10}$. High I/O ratios observed for $PM_{2.5}$ (6.6) justified the previous results, confirming that tobacco smoke was the important source of indoor PM, significantly increasing concentrations of particles in $PM_{2.5}$ fraction mainly.

4.3.2 Carcinogenic components

The indoor and outdoor concentrations of carcinogenic components, namely PAHs and metals such as As, Cr, Ni, Cd and Pb were also studied. As these components were predominantly present in $PM_{2.5}$, as shown in Sections 4.1 and 4.2, in the following comparisons their concentrations in $PM_{2.5}$ were considered.

The levels of carcinogenic metals were significantly higher outdoors being influenced by traffic emissions than at indoor non-smoking (reference) places. For all considered metals, the observed values of I/O ratios were lower than 1, ranging from 0.15 for Pb to 0.28 for Cr. These results indicate that there were not any significant sources of carcinogenic metals indoors. Confirming the previous results the carcinogenic metals in reference $PM_{2.5}$ resulted from penetrations of outdoor particles, i.e. from traffic emissions.

The total concentration of nine carcinogenic PAHs (naphthalene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, and dibenzo[a,l]pyrene) was 6 ± 4 ng m^{-3} in reference indoor (non-smoking) $PM_{2.5}$ whereas it was 10 ± 6 ng m^{-3} outdoors. The concentrations of individual PAHs indoors were approximately 40% lower, being in agreement with other studies (Srogi, 2007). Accordingly, the values of I/O ratios of carcinogenic PAHs were lower than 1, ranging from 0.21 for indeno[1,2,3-cd]pyrene to 0.73 for benz[a]anthracene. Therefore, it was possible to conclude that indoor PAHs associated with PM resulted from contribution of outdoor emissions, i.e. traffic. Confirming these results, it was also observed that PAHs with 5-6 rings were the most abundant compounds

indoors accounting for 81%; previously some authors reported that infiltration of outdoor air is the main reason for the indoor prevalence of PAHs with high molecular weight (Li et al., 2005). Furthermore, as it can be observed in Figure 4.34, the composition profiles of PAHs influenced by traffic emissions were almost identical to those of indoors, namely for benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene, and benzo[a]pyrene. These compounds are indicators of traffic emissions and their similar occurrences justified the previous results concluding that traffic emissions significantly contributed to indoor PM.

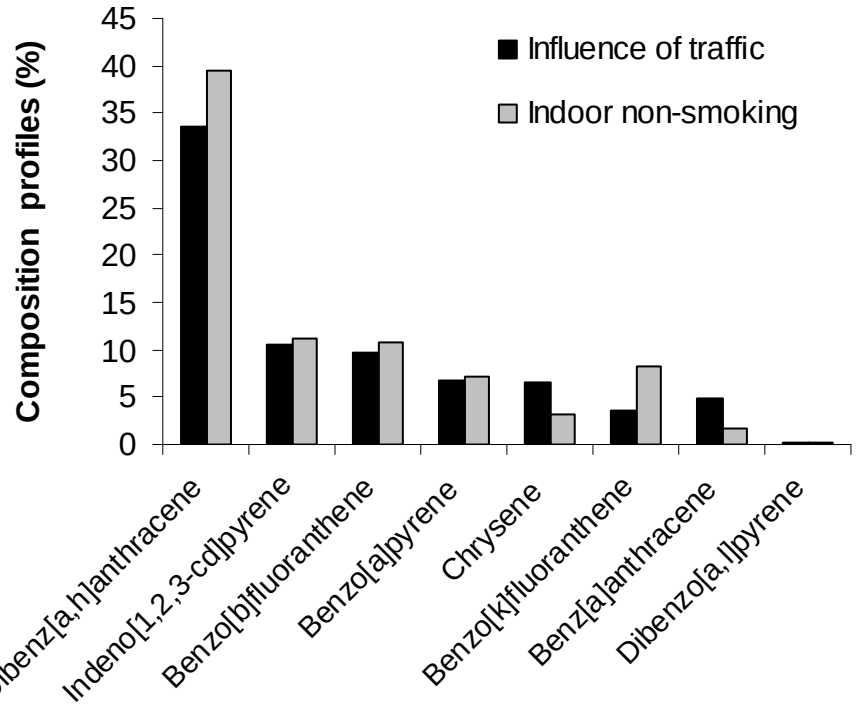


Figure 4.34 Composition profiles of PAHs influenced by traffic emissions (outdoor) and indoors.

The outdoor and indoor concentrations of carcinogenic components were also compared for indoor environments influenced by tobacco smoke. When influenced by tobacco smoke, $PM_{2.5}$ contained Cr, Ni, Pb but also As and Cd. These two elements were the most abundant ones, accounting for 85% of the total concentration of all carcinogenic metals. As and Cd occurred only in indoor place influenced by tobacco smoke, thus showing its strong contribution to these two carcinogenic metals. Unlike As and Cd, the concentrations of Cr, Ni, and Pb were lower when influenced by tobacco smoke than under influence of traffic emissions. Accordingly, the means of I/O ratios for these three metals were lower than 1,

ranging from 0.20 for lead to 0.72 for Ni. These results indicate that although Cr, Ni, and Pb were previously associated with influence of tobacco smoke, their respective presence indoors were probably due to the contribution of outdoor particles.

When influenced by tobacco smoke the total concentration of carcinogenic PAHs increased to 52 ± 31 ng m^{-3}. As expected the I/O ratios of carcinogenic PAHs were higher than 1, ranging up to 22 for chrysene. These results confirm that PAHs originated from indoor sources, i.e. from tobacco smoke. It was also observed that when influenced by tobacco smoke, especially PAHs with 4 rings increased significantly in comparisons with outdoors. The highest differences were observed for chrysene; when influenced by tobacco smoke concentrations of chrysene were 2100% higher than when influenced by traffic emissions. Accordingly the composition profiles of carcinogenic PAHs influenced by tobacco smoke and traffic emissions differed considerably as demonstrated in Figure 4.35.

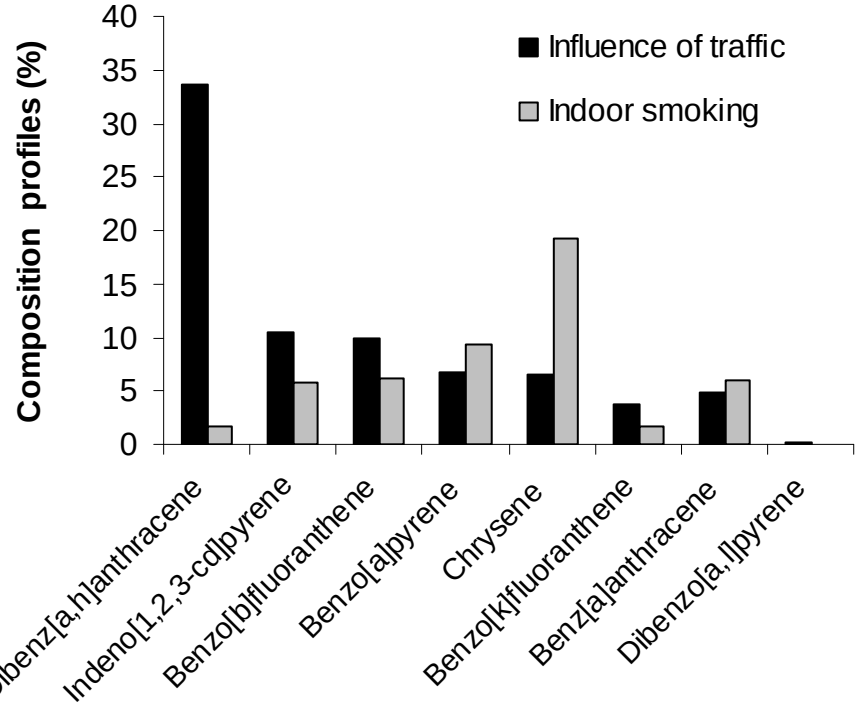


Figure 4.35 Composition profiles of carcinogenic PAHs influenced by traffic emissions and tobacco smoke.

4.3.3 Conclusions

The obtained results allowed concluding that:

- The concentrations of carcinogenic components were at indoor non-smoking place lower than those outdoors being influenced by traffic emissions.
- When influenced by tobacco smoke the concentrations of carcinogenic components were higher indoors than outdoors.
- The carcinogenic components at non-smoking indoor places resulted from contribution of traffic emissions.
- The carcinogenic components at indoor places influenced by tobacco smoke mainly resulted from that source.

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5. Conclusions

Regarding the influence of traffic emissions, the obtained results allowed concluding that:

- Traffic emissions increased 370-680% PM_{10} concentrations and 360-750% $PM_{2.5}$ concentrations.
- The elements originated mostly from anthropogenic activities were predominantly present in $PM_{2.5}$ fraction; the elements mostly originated from crust predominantly occurred in the particles of $PM_{2.5-10}$.
- At the sites influenced by traffic emissions, particle metal contents were for PM_{10} 15-4600% higher and for $PM_{2.5}$ 110-2600% higher than at the backgrounds sites; traffic emissions increased greatly the levels of metals.
- At the sites influenced by traffic emissions the levels of organic carbon were, respectively, 240-480% and 290-390% higher for PM_{10} and $PM_{2.5}$, whereas concentrations of elemental carbon increased 500-900% and 490-740% for PM_{10} and $PM_{2.5}$, respectively.
- Traffic emissions, being originated from diesel engines mainly, significantly increased PAHs in PM_{10} and $PM_{2.5}$:
    - Carcinogenic compounds (naphthalene, chrysene benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene) and dibenzo[a,l]pyrene increased 2400% and 3000% for PM_{10} and $PM_{2.5}$, respectively; these nine

compounds represented, respectively, 68% and 74% of total PAHs. These carcinogenic compounds as well as other PAHs were mainly present in $PM_{2.5.}$

Regarding the influence of tobacco smoke, the obtained results allowed concluding that:

- Tobacco smoke strongly increased PM concentrations, this increase being higher for particles of smaller sizes: 270-560% for PM_{10} and 320-680% for $PM_{2.5}$.
- Tobacco smoke increased the total concentrations of five carcinogenic elements (Cr, Ni, As, Cd and Pb) by 1100-3500% for PM_{10} and 840-2200% for $PM_{2.5}$, respectively.
- The carcinogenic elements as well as other elements associated with tobacco smoke (S, K, Zn) were predominantly present in $PM_{2.5}$; the elements mostly originated from building erosion (Mg, Al, Si, Ca and Ti) predominantly occurred in the $PM_{2.5-10}$.
- Tobacco smoke increased the carbonaceous species in PM_{10} and $PM_{2.5}$:
    - Concentrations of elemental carbon were 15-200% and 15-180% higher in PM_{10} and $PM_{2.5}$, respectively.
    - Organic carbon concentrations were 290-500% and 300-590% higher in PM_{10} and $PM_{2.5}$, respectively.
- Tobacco smoke increased the concentrations and distributions of PAHs in PM_{10} and $PM_{2.5}$:
    - Carcinogenic PAHs (naphthalene, chrysene benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene) and dibenzo[a,l]pyrene were 780% and 770% higher for PM_{10} and $PM_{2.5}$, respectively.
        - At the site influenced by tobacco smoke chrysene was the most abundant compound of all PAHs in PM_{10} and $PM_{2.5}$, being followed by benzo[a]pyrene (the most known carcinogen with concentrations 1300% higher in both PM), naphthalene and benz[a]anthracene.
        - At reference (non-smoking) site dibenz[a,h]anthracene (indicator of traffic emissions with high carcinogenic potency) was the most abundant PAH in both PM, with concentrations about 50% higher than at the site influenced by tobacco smoke.
        - Even at the reference site carcinogenic PAHs were present in PM_{10} and $PM_{2.5}$, originated from traffic emissions.

- Carcinogenic PAHs represented 56% and 55% of total PAHs for the PM_{10} and $PM_{2.5}$ at the site influenced by tobacco smoke, respectively.
- Carcinogenic PAHs represented 80% and 81% of total PAHs in reference PM_{10} and $PM_{2.5}$, respectively.

- The carcinogenic compounds as well as other PAHs were mainly present in $PM_{2.5}$.

Considering that carcinogenic components were predominantly present in particles of smaller sizes, the obtained conclusions justify the strong risks associated with exposure to traffic emissions and tobacco smoke. To protect public health it is necessary to establish the limits for concentrations of the carcinogenic components in particles of smaller sizes (i.e. $PM_{2.5}$) in both outdoor and indoor air; in adequate form these limits have not been established anywhere yet.

The absolute values of carcinogenic compounds were higher at the places influenced by tobacco smoke than at those influenced by traffic emissions; however, the presence of carcinogenic components from traffic emissions at non-smoking residences shows the strong influence of these emissions on public health. Therefore, the reduction of traffic emissions is particularly important; unlike tobacco smoke it is not possible to reduce exposure to traffic emissions voluntarily as their presence is ubiquitous. Furthermore, when the protection of public health is aimed, traffic emissions should be obligatory considered.

The results obtained in this work are relevant for development of strategies to protect public health and to support future epidemiological studies evaluating passive smokers and populations affected by traffic emission sources.

In order to better understand the health impacts of PM, the future research should focus on $PM_{2.5}$ and on even smaller “ultrafine” particles. The harmful components of these particles should be further addressed, namely related to human carcinogenicity. Concerning to PAHs, their seasonal differences in PM should be dealt with and the personal exposures to these carcinogenic compounds should be observed. Finally, large-scale epidemiologic studies of PM and the documentation of the respective health effects are needed to obtain sufficiently informative data.

APPENDIX

A.PM sampling

A.1 Sampling apparatus

A.1.1 Technical specifications of TCR TECORA Bravo H2 constant flow sampler

Flowrate range (l min^{-1})	1-60
Double flowrate adjustment	x
Pressure drop meter	x
Dry mas meter, resolution 0,2 l	x
Forced air cooling system	x
Analog thermometer (0-80 °C)	-
Pump type	piston
Free inlet flowrate (l min^{-1})	80
mP Controller	x
Fast inlet	x
Power supply 220V - 50 Hz	x
Size (h x l x p) (mm)	330 x 315 x 330
Weight (kg)	14

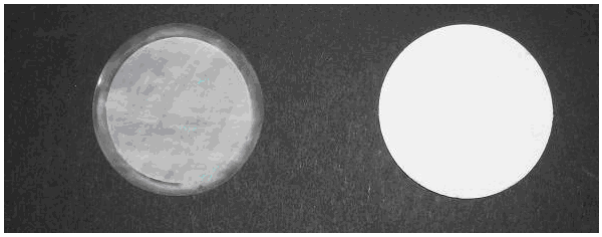
A.1.2 Sampling head

A.1.3 Components of sampling head

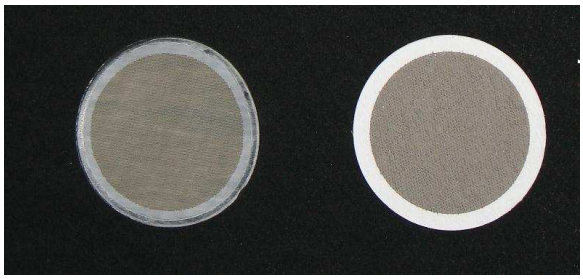
A.1.4 Filter holder

A.2 Filters

Non-exposed PTFE and quartz fibre filters.



Exposed PTFE and quartz filters (traffic emissions).



Exposed PTFE and quartz filters (tobacco smoke).

A.3 Sampling sites

Monitoring site Bc_1, north of Portugal, winter 2004-2005.

Monitoring site Tr_2, Porto, summer 2005.